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Chemical Kinetics. The Temperature Dependence of the Energy of Activation. The Entropy and Free Energy of Activation

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I. INTRODUCTION

ALL modern theories of reaction velocity recognize the importance of precise determinations of the energy of activation. For this purpose the temperature coefficients of the velocity of gaseous reactions and of non-ionic reactions in solution have been studied in some detail.

Comparable data for ionic reactions are exceedingly meager and the theoretical implications have been virtually neglected. The activation energies of ionic reactions are of particular interest for the following reasons.

The partial molal heat capacities of ions are large negative[1, 2] values, which depend upon the electric charge, the total concentration, and certain specific factors arising from interaction with the solvent. Since the temperature dependence of the energy of activation involves heat capacities, it is conceivable for reactions between ions that $E_{act.}$ may not be independent of temperature. The approximation that $E_{act.}$ is constant is almost universally accepted in integrating the Arrhenius equation.

Interionic attraction modifies the rates of ionic reactions by changing the number and character of the effective collisions, a circumstance which emphasizes the necessity for considering the orientation of the molecules at collision.[3, 4]

The experimental evidence that activation energies of ionic reactions are dependent upon both temperature and concentration will be given in later papers of this series. The present paper will treat the simpler case of non-ionic reactions from the viewpoint of the statistical foundations of the Arrhenius equation; the derivation and limitations of the Brönsted equation; the validity of collision theories; and the experimental evidence for the temperature dependence of $E_{act.}$ in non-ionic reactions.

II. THE ARRHENIUS EQUATION AND ITS DERIVATIVES

We start with the Arrhenius equation in the form

$$\frac{d \ln k_2}{dT} = \frac{1}{2T} + \frac{\bar{\epsilon} - \bar{\epsilon}}{kT^2} = \frac{1}{2T} + \frac{E_{act.}}{RT^2}, \qquad (1)$$

which R. C. Tolman[5] has shown follows from statistical mechanics for a bimolecular reaction. To emphasize the salient features for later discussion, we give the simpler development valid for a unimolecular reaction and refer the reader

[1] La Mer and Cowperthwaite, J. Am. Chem. Soc. **55**, 1004 (1933).
[2] Randall and Rossini, ibid. **51**, 323 (1929).
[3] La Mer and Kamner, J. Am. Chem. Soc. **53**, 2832 (1931).
[4] La Mer, Chem. Rev. **10**, 179 (1932).
[5] R. C. Tolman, *Statistical Mechanics*, Chem. Catalog Co., pp. 259–69, 1927.

to Tolman and Kassel's monographs[6] for details of the origin of the term $\frac{1}{2}T$ in the bimolecular case.

Consider a system of molecules of index i, distributed in various quantum levels having the energies ϵ_i and the statistical weights p_i. The molecules in the higher *reactive* quantum states will be indicated by the index j, and will be assigned undetermined specific individual rate (reactivity) constants k_j. The number of molecules, n_j, in the j^{th} quantum state is

$$n_j = n p_j e^{-\epsilon_j/kT} / \sum_i p_i e^{-\epsilon_i/kT}, \tag{2}$$

where kT is the Boltzmann constant times the absolute temperature.

The overall, measurable, specific rate constant k_1, is then

$$k_1 = -\frac{1}{n}\frac{dn}{dt} = \frac{\sum_j k_j p_j e^{-\epsilon_j/kT}}{\sum_i p e^{-\epsilon_i/kT}}. \tag{3}$$

Logarithmic differentiation yields

$$\frac{d \ln k_1}{dT} = \frac{1}{kT^2}\left[\frac{\sum_j \epsilon_j k_j p_j e^{-\epsilon_j/kT}}{\sum_j k_j p_j e^{-\epsilon_j/kT}} - \frac{\sum_i \epsilon_i p_i e^{-\epsilon_i/kT}}{\sum_i p_i e^{-\epsilon_i/kT}}\right] \tag{4}$$

$$= (1/kT^2)[\bar{\bar{\epsilon}} - \bar{\epsilon}] = E_{\text{act.}}/RT^2. \tag{5}$$

The last term in the bracket is the average energy $\bar{\epsilon}$ of *all molecules, while the first term refers to the average energy of the molecules in j states, in which the usual weight factor p_j has been replaced by $k_j p_j$.* This means that $\bar{\bar{\epsilon}}$ *refers* to the average energy of the *molecules which react.* The quantity $N(\bar{\bar{\epsilon}} - \bar{\epsilon})$ will be defined as the energy of activation per gram mole.

Since the reacting molecules constitute but a minute fraction of the total, no sensible error is made by identifying $\bar{\epsilon}$ as the average energy of those molecules which do not react.

To obtain an expression for the variation of the energy of activation with temperature, we differentiate Tolman's expression, Eq. (4), and obtain a quantity $C_{\text{act.}}$ which we shall call the *heat capacity of activation.*

$$d[kT^2(d \ln k_1)/dT] = d(E_{\text{act.}})/dT = C_{\text{act.}}. \tag{6}$$

The differentiation yields:

$$\frac{d(E_{\text{act.}})}{dT} = \frac{1}{kT^2}\left\{\left[\left(\frac{\sum_j \epsilon_j^2 k_j p_j e^{-\epsilon_j/kT}}{\sum_j k_j p_j e^{-\epsilon_j/kT}}\right) - \left(\frac{\sum_j \epsilon_j k_j p_j e^{-\epsilon_j/kT}}{\sum_j k_j p_j e^{-\epsilon_j/kT}}\right)^2\right] - \left[\left(\frac{\sum_i \epsilon_i^2 p_i e^{-\epsilon_i/kT}}{\sum_i p_i e^{-\epsilon_i/kT}}\right) - \left(\frac{\sum_i \epsilon_i p_i e^{-\epsilon_i/kT}}{\sum_i p_i e^{-\epsilon_i/kT}}\right)^2\right]\right\} \tag{7}$$

$$dE_{\text{act.}}/dT = (1/kT^2)\{[\bar{\bar{\epsilon}}^2 - \bar{\bar{\epsilon}}^2] - [\bar{\epsilon}^2 - \bar{\epsilon}^2]\}. \tag{8}$$

$$= (\bar{C}_{j(\text{act.})} - \bar{C}_i) = C_{\text{act.}} \tag{8a}$$

In the case of heat capacities, the bar refers to the partial molal quantity, whereas with the energies ϵ it refers to the average.

The quantity $[\bar{\epsilon}^2 - \bar{\epsilon}^2]$ is the difference between the mean of the squares of the energies of all the molecules and the square of their mean energy, and consequently represents the *fluctuations*[7, 8] in their energy. $[\bar{\epsilon}^2 - \bar{\epsilon}^2]/kT^2$ is equal to the calorimetrically measurable partial heat capacity of all the molecules, which heat capacity is indistinguishable from that of the non-reacting molecules.

By the same token $[\bar{\bar{\epsilon}}^2 - \bar{\bar{\epsilon}}^2]/kT^2$ represents the partial heat capacity of the *molecules which react,* but differs from the thermodynamic heat capacity of the molecules in activated states since each p_j has been replaced by $k_j p_j$ in the averaging process.

The integration of Eq. (1) under the assumption that $E_{\text{act.}}$ is independent of T is equivalent to setting Eq. (8) equal to zero, i.e., $\sum \bar{C}_{\text{act.}} = \bar{C}_{X(\text{act.})} - (\bar{C}_A + \bar{C}_B)$ is zero for the bimolecular reaction $A + B \rightleftarrows X \rightarrow R$.

When heat capacities are neglected free energy and total energy become indistinguishable. This approximate treatment, corresponding in the integrated form to

$$\ln k = 2.3B - E_{\text{act.}}/RT \tag{9}$$

has met with considerable success in the treat-

[6] L. S. Kassel, *Kinetics of Homogeneous Gas Reactions,* Chem. Catalog Co., pp. 19–26, 1932.

[7] R. H. Fowler, *Statistical Mechanics,* Cambridge, 1929; Eq. (1435), p. 513.

[8] J. W. Gibbs, *Statistical Mechanics,* Longmans, 1928; (Chap. VII, Eq. (205), Chap. XIV and XV).

ment of gaseous reactions, notably in the hands of Hinshelwood.[9]

The correction which we introduce by considering the temperature dependence of $E_{act.}$ can be understood better by pointing out the close analogy to the corresponding thermodynamic process of calculation. The integral

$$\int \frac{E_{act.}}{T^2}\,dT = -\frac{E_{act.}}{RT} + \int \left(\frac{\partial E_{act.}}{\partial T}\right) d \ln T.$$

The last term by definition is equal to $\int C_{act.} d \ln T$, which is in complete analogy with the thermodynamic expression for the entropy S; namely, $S = \int (\partial E/\partial T) d \ln T$. We therefore consider it entirely justifiable to speak of the *entropy of activation*, $S_{act.}$, provided it is kept clearly in mind that $S_{act.}$ contains the kinetic factors k_j found in the first terms of Eq. (7).

It cannot be emphasized too strongly, that to neglect the entropy of activation, as is the case, (Eq. 9), when $E_{act.}$ is taken independent of T, has no more justification than would be the omission of the entropy terms involved in the calculation of a thermodynamic equilibrium.

In the case of electrolytes the assumption that $C_{act.} = 0$ is certainly not justified *a priori*. We shall accordingly integrate under the assumption that $E_{act.}$ is a function of T, even though we cannot take full advantage of the improvement produced; thus,

$$\ln k = \text{constant} + \tfrac{1}{2} \ln T - \frac{F_{act.}}{RT}. \qquad (10)$$

The free energy of activation, $F_{act.} = E_{act.} - TS_{act.} = \bar{F}_{X(act.)} - (\bar{F}_A + \bar{F}_B)$, where the bars refer to the chemical potentials. The subscript, activation, is retained for the X or critical state to emphasize that $\bar{F}_{X(act.)}$ contains the k_j factors and therefore refers to the molecules which react, whereas $\bar{F}_A$ and $\bar{F}_B$ are free from k_j factors. The X state is the rate determining intermediate state.

The constant in (10) is evaluated by comparison with $\ln k$ when $F_{act.} = 0$. For a process without activation, every collision will be fruitful and the *constant* $= \ln Z^0 - \frac{1}{2} \ln T$. For a dilute gas, Z^0 is the gas kinetic constant for the number of collisions per unit of time $= 2\sigma_1\sigma_2[2\pi RT(m_1+m_2)/m_1m_2]^{\frac{1}{2}}$, and has the dimensions of a frequency (time^{-1}).

III. Systems with Interaction. The Bronsted Equation

To account for changes in the medium with changes in concentration, Bronsted[10] generalized the classical theory of reaction velocity by introducing the activity coefficients of the reactants and the critical complex in terms of a kinetic factor $f_A f_B / f_X$. His theory although most useful in treating ionic reactions is by no means so limited. The foundation of his equation has been the subject of much discussion[11, 12, 13, 4] and a direct derivation is highly desirable.

The statistics, upon which Eqs. (1–7) are founded, were developed primarily for perfect gas mixtures. For such systems, the quantities ϵ_i, ϵ_j and k_j are independent of both temperature and concentration. However, when we consider more concentrated systems, and particularly the liquid state, ϵ_i, ϵ_j and presumably also k_j will depend upon the mutual energy of the molecules. These quantities may consequently depend upon the concentration and temperature, since the energy of each molecular system depends upon the configuration of all other molecular systems in the assembly.

The ensemble[14] method of Gibbs, in contrast to the classical development of Boltzmann recognizes the fundamental character of the problem of interaction energy by including it in the conditional equations employed in deriving the

[9] C. N. Hinshelwood, *Kinetics of Homogeneous Gas Reactions*. Oxford, 1929, p. 42, where the view is advanced that "if when log k is plotted against $1/T$ a straight line is not obtained, this is an almost certain indication that the observed reaction is a composite one made up of two or more concurrent reactions differently influenced by temperature." Cf. Kassel, reference 6, pp. 149–56, where the data on hydrogen iodide have been subjected to a critical reexamination and the conclusion drawn that $E_{act.}$ increases with temperature.

[10] Bronsted, Zeits. f. physik. Chemie **102**, 169 (1922); **115**, 337 (1925).

[11] Bjerrum, Zeits. f. physik. Chemie **108**, 82 (1924); **118**, 251 (1925).

[12] Christiansen, Zeits. f. physik. Chemie **113**, 35 (1924).

[13] Skrabal, Zeits. f. physik. Chemie **B3**, 247 (1929).

[14] W. Gibbs, reference 8, pp. 36–7. Consult also Fowler, reference 7, where certain aspects of the problem are stated but not solved, pp. 164–5, 181–2, 307.

distribution laws. Unfortunately an explicit solution by the Gibbs method encounters unsurmountable mathematical difficulties, so that for the present we must abandon a rigorous statistical derivation and resort to thermodynamic analogies as our guide. In a thermodynamic procedure the correction factors due to interaction will enter as the empirically determined activity coefficients.

In this section we shall drop, temporarily, the subscript, activation, to simplify the notation, but without losing sight of the kinetic character of such quantities. In analogy with thermodynamic procedure we decompose $\bar{F}$ into an ideal part $\bar{F}_{\text{id.}}$ and a non-ideal or excess part, $\bar{F}_e$ arising from interaction effects.

Thus

$$\bar{F}=\bar{F}^0(T)+RT\ln f(T,c) \qquad (11)$$

$$=\bar{F}_{\text{id.}} + \bar{F}_e(T,c), \qquad (11a)$$

equations which serve as definitions for the activity coefficient, f. The small c will refer to concentration, the large capital C to ideal heat capacity.

The omission of the term $RT\ln c$ for $\bar{F}_{\text{id.}}$ requires justification. In evaluating the free energy of activation, we are concerned only with the individual energy levels which are independent of concentration for the perfect gas mixture. Terms of the type $RT\ln c$ arise from the disorder which occurs when molecules of different types are mixed but not when like types are mixed (Gibbs paradox). In the present instance, the integration producing $\bar{F}_{\text{id.}}$ involves only quantities which are characteristic of the energies of each individual group of molecules, and consequently no terms of the type $RT\ln c$ can appear in the expression for $\bar{F}$. This may be more evident by considering the formal analogy to the previously mentioned thermodynamic integral $S=\int C d\ln T$, where C represents the ideal heat capacity, which of course cannot produce the term $R\ln c$, which arises from the Gibbs paradox.

On the other hand, the $RT\ln f$ term originates from the integration of the corresponding non-ideal heat capacity term produced by interaction effects whereby an excess entropy and a corresponding excess free energy result.

Introducing (11) and (11a) in (10) yields

$$\ln k=\ln Z^0-\sum\bar{F}^0/RT-\sum\bar{F}_e/RT, \qquad (12)$$

$$k=Z^0\exp\left(\frac{-[\bar{F}_{X(\text{act.})}-(\bar{F}_A+\bar{F}_B)]}{RT}\right)\frac{f_Af_B}{f_X}. \qquad (13)$$

As a result, we have Bronsted's Eq. (14)

$$k=k_0(f_Af_B)/f_X \qquad (14)$$

which can also be written

$$k=k_0e^{-Fe/RT}$$

when k_0 is set equal to

$$Z^0\exp\left(\frac{-[\bar{F}_X{}^0-(\bar{F}_A{}^0+\bar{F}_B{}^0)]}{RT}\right)=Ze^{-F^0/RT}. \qquad (15)$$

The choice of the constants $\bar{F}_X{}^0$, $\bar{F}_A{}^0$, $\bar{F}_B{}^0$, which are independent of concentration, implies that f_Af_B/f_X is normalized as unity for the reference solvent; hence any dependence upon concentration arising from a change in the medium (for example, neutral salt addition) finds expression in terms of the activity coefficients. In passing from the gaseous to new liquid states of reference, any purely kinetic factors such as viscosity, which can affect the numerical value of Z^0 will have to be taken into account.[15, 16] k_0 thus corresponds to the specific velocity constant in the reference solvent when freed from all interactions between A, B and X *except idealized collisions*, but not from interaction with the solvent. If relative activity coefficients are normalized for each new solvent, the effect of interaction with the solvent will appear in the values of $\bar{F}_X{}^0$, $\bar{F}_A{}^0$, $\bar{F}_B{}^0$ required for each solvent.

We believe that in our method of approach we have given for the first time a clear meaning to the quantities f_X or $\bar{F}_X{}^0$, by emphasizing the limitations which must be placed upon all attempts to interpret f_X as a pure thermodynamic quantity, for example, when f_X is replaced by a simple theoretical expression like the Debye limiting law which obviously cannot contain k_j factors.

Only in the special case where the k_j values are all equal or only one j level is involved, do the k_j values cancel in the averaging process, so that f_X

[15] Jowett, Phil. Mag. **8**, 1059 (1929).

[16] Moelwyn-Hughes, J. Chem. Soc. (London) 1932, 95.

can be interpreted as a pure thermodynamic quantity. Equality of the k_j factors is unlikely. On the other hand, if the reaction proceeds through a single quantum state j, then by Eqs. (7) and (8), the heat capacity of the reacting molecules is zero and $C_{act.} \leq 0$; i.e., $E_{act.}$ must be constant or decrease with rising temperature. Consequently if $E_{act.}$ increases with T we have convincing evidence that the reaction proceeds through more than one reactive level and the X state is multiple.

As a corollary of our theory we have the proposition that whenever $E_{act.}$ rises with temperature, substitution of a thermodynamic expression (f. ex. (D.H.L.)) for f_X is illegitimate. Even if $C_{act.} \leq 0$, we cannot be certain that the X state is not multiple, since a finite heat capacity for the reacting molecules may be counterbalanced by the heat capacity of the non-reacting molecules.

Hinshelwood's statement[9] that inconstancy of $E_{act.}$ indicates a composite reaction is, of course, true when considered from the standpoint of paths involving different quantum levels, but from the context his statement is obviously intended for the appearance of side reactions involving the production of new chemical species or entirely new mechanisms in the chemical sense.

IV. Entropy of Activation, and the Collision Theory

Recently Moelwyn-Hughes[17] has extended the simple collision theory of gaseous reactions to solutions. He determines $E_{act.}$ from measurements of the temperature coefficient, and from the gas kinetic value of Z, using reasonable values of the molecular radii σ_1, and σ_2 he computes a theoretical value of k.

For a large number of reactions the calculated value of k differs from the observed by a factor of only 10 to 100. Consequently Moelwyn-Hughes concludes that the simple collision theory is applicable to solutions.

There are two reasons why this is not convincing: (1) For a group of reactions (mostly bimolecular associations), Moelwyn-Hughes finds k is 10^4 to 10^9 times smaller than that calculated, while our unpublished results for the β-bromopropionate-thiosulfate reaction yield rates which are many times greater than those calculated from his theory, in spite of the fact that the repulsive action of the electric charges might be expected to reduce the rate. (2) Moelwyn-Hughes' theory neglects completely the possibility of an entropy of activation ($S_{act.}$) resulting from a temperature dependence of $E_{act.}$.

By comparing Eqs. (9) and (10), we find

$$B = \log Z^0 + S_{act.}/2.3R, \tag{16}$$

where $S_{act.}$ is equal to

$$\int_0^T C_{act.} d \ln T.$$

The Hinshelwood-Moelwyn-Hughes theory makes the tacit assumption that the heat capacities of activation of the reacting and of the non-reacting molecules remain *identical down to absolute zero*. There is no valid theoretical reason for such an assumption, especially when one considers that for such minor differences as that of proton spin, the heat capacities of ortho and para hydrogen differ considerably at low temperatures,[18] and consequently possess different entropies at room temperature.

There are six important cases connecting $E_{act.}$, $S_{act.}$, $C_{act.}$, Z^0 and B.

Case I. $C_{act.} > 0$ at all temperatures; $E_{act.}$ rises with increasing T; $S_{act.} > 0$, and $B > \log Z^0$.

Case II. $C_{act.} > 0$ in the range of experimental measurement (high T) but $C_{act.} \ll 0$ at lower temperatures. Then $S_{act.} < 0$ and $B < \log Z^0$ in the range of investigation.

Case III. $C_{act.} < 0$ at all temperatures. $E_{act.}$ decreases; $S_{act.} < 0$; $B < \ln Z^0$.

Case IV. $C_{act.} < 0$ at high T, but $C_{act.} \gg 0$ at low T. $S_{act.} > 0$ and $B > \log Z^0$ in range of measurement.

Case V. Condition for the validity of Arrhenius assumption. $C_{act.} = 0$ within experimental error in temperature range of measurement; $S_{act.} > 0$ or

[17] Moelwyn-Hughes, Chem. Rev. **10**, 241 (1932); Nature **129**, 316 (1932); J. Chem. Soc. (1932) 95; with Hinshelwood, (1932) 230; with Rolfe, (1932) 241.

[18] Eucken, Hiller and Clusius, Zeits. f. physik. Chemie **B4**, 142 (1929); *Treatise on Physical Chemistry*, Van Nostrand (1931), p. 305.

$S<0$ depending upon behavior of $C_{act.}$ at low T. $B>\log Z^0$, or $B<\log Z^0$.

Case VI. Condition for the validity of the Hinshelwood-Moelwyn-Hughes theory. $C_{act.}=0$ at all temperatures or varies in such a way at low temperatures that $S_{act.}=0$; then $B=\log Z^0$.

V. Experimental Data

It is unfortunate that $E_{act.}$ cannot be measured at low temperatures to reveal to what extent the neglect of the entropy of activation accounts for the failure of the collision theory. However, a critical examination of the best existing data discloses that $E_{act.}$ varies with T in the range of measurement. All values of $E_{act.}$ have been recalculated from original data by using $R=1.9885$ calories and $T=273.13$ for the ice point. B is in minutes.

Table I refers to Wiig's results for the decomposition of acetone-dicarboxylic acid from 0 to 60°C at 10° intervals. No statement of the reproducibility of the individual measurements is given, but since with two different analytical techniques k checks to 1 percent (± 300 calories in $E_{act.}$) the probable error in a series for the same technique may be less. Dr. Wiig informs me that a reexamination of his original data shows that the average deviation from the mean at each temperature is about 1 percent.

The reversal in sign of $C_{act.}$ would be disregarded were it not uniformly exhibited by Segaller's extensive studies on the reaction between primary, iso- and secondary alkyl iodides with sodium phenoxide. Our calculations for the primary iodides, which cover a 50° range are given in Table II. Segaller called attention to the fact that his measurements at higher temperature did not fall on a straight line for a log k, $(1/T)$ plot, and contends the discrepancy cannot be due to experimental error.

Table I. *The decomposition of acetone-dicarboxylicacid in water.**

B(1st order); time units minutes^{-1}.

t°C	B	$E_{act.}$	$C_{act.}$
0–10°	13.58	22749	
			24
10–20	13.77	22993	
			35
20–30	14.03	23340	
			49
30–40	14.37	23826	
			−35
40–50	14.13	23477	
			−23
50–60	14.00	23244	

* Wiig, J. Phys. Chem. **32**, 961 (1928); **34**, 596 (1930).

In Fig. 1 are plotted the values of $C_{act.}$ calculated from Wiig's data (J. Am. Chem. Soc. **53**, 4729 (1930) Table VI) for $k_{25°}/k_{15°}$ and $k_{35°}/k_{25°}$ for the decomposition of citric acid in concentrated sulfuric acid. With the exception of the two points at low water content, it is very interesting to note that with increasing water content, $C_{act.}$ changes quite uniformly from negative to positive values. This means that the addition of water increases the heat capacity of the reactive complex.

In Table III are given calculations from G. M. Murphy's measurements on the diacetone-alcohol reaction, considered as a bimolecular

Table II. *The reaction of sodium phenoxide with primary alkyl iodides.**

Solvent, absolute ethanol. B(2nd order); $B=$ min.$^{-1}$.

Alkyl iodide	$t=30.1°$–$42.5°$ E	B	$t=42.5°$–$58.5°$ E	B	$E_{50.3°}-E_{36.3°}$	$t=58.5°$–$80.1°$ E	B	$E_{69.3°}-E_{50.3°}$
Methyl	20,945	13.28	21,876	13.92	(931)	——	——	——
Ethyl	21,067	12.71	21,604	13.08	537	21,263	12.86	−341
Propyl	21,508	12.60	22,048	12.98	540	21,561	12.65	−487
Butyl	20,560	11.92	22,197	13.05	637	21,551	12.62	−646
Amyl	20,696	11.63	22,353	12.79	657	21,385	12.15	−968
Hexyl	20,622	11.94	22,175	13.01	553	21,770	12.75	−405
Heptyl	20,834	12.07	22,183	13.00	549	21,958	12.85	−225
Octyl	21,199	12.31	22,364	13.12	(1,165)	22,050	12.90	−314
Hexadecyl	21,307	12.37	22,188	12.98	(881)	22,146	12.96	−42
Average $C_{act.}$					41 cals. deg.$^{-1}$			−2 to −51 cals. deg.$^{-1}$

* D. Segaller, J. Chem. Soc. **105**, 106 (1914).

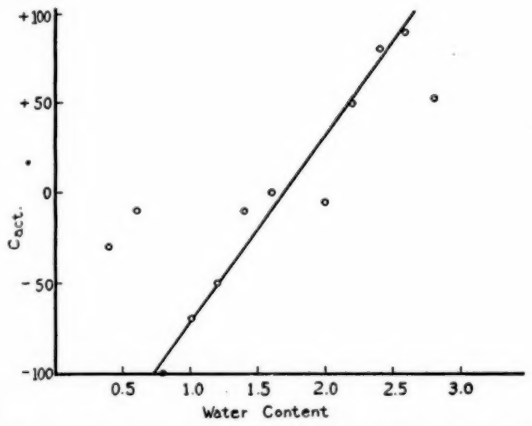

FIG. 1. Heat capacity of activation in calories/deg. mole (15–25°; 25–35°) for the water inhibited reaction. Thermal decomposition of citric acid in concentrated sulfuric acid as function of water content. Data by Wiig, J. Am. Chem. Soc. **53**, 4729 (1930), Table VI.

TABLE III. *The decomposition of diacetone-alcohol by 0.1M sodium hydroxide. E precise to ± 0.7 percent.**

B(mols. liter^{-1} min.$^{-1}$ is computed on the basis of a bimolecular reaction between NaOH and diacetone-alcohol. *B*(1st order) = *B*(2nd order) − 1. Log $Z°(\sigma = 5A°) = 13.36$ (min.$^{-1}$).

Solvent Water+0.1*M* NaOH		*E* 20°–30°	*B*	*E* 25°–35°	*B*	$C_{act.}$
0%	CH_3OH	17,040	12.19	18,098	12.94	211
10%	"	17,638	12.50	18,670	13.20	206
20%	"	18,311	12.85	19,481	13.70	234
30%	"	18,525	12.88	19,694	13.74	234
40%	"	18,852	12.99	19,822	13.71	194
50%	"	19,349	13.23	20,080	13.78	146
60%	"	19,776	13.42	20,578	14.03	160

*G. M. Murphy, J. Am. Chem. Soc. **53**, 977 (1931).

reaction with 0.1M NaOH. A precision of 0.7 percent or 126 calories is claimed for $E_{act.}$. It will be noted that $E_{act.}$ increases over a ten degree interval by roughly 1000 calories or eight times the probable error. A calculation based upon 5° intervals indicates decreasing values of $C_{act.}$ with increasing T as in Table II. This reaction is now being investigated in this laboratory over wider ranges of temperature to verify this deduction.

VI. Concluding Remarks

After this paper was practically completed for publication the interesting papers of Scheffer[19] and Brandsma[20] were discovered, where the importance of considering the free energy and entropy of the intermediate state is emphasized. Their viewpoint differs from ours in at least one important respect. They consider that these pure thermodynamic properties determine the rate, whereas we consider the rate determining properties of the intermediate state to be in general kinetic quantities, since they contain k_j factors. Except for this difference, their thesis that part of the entropy of activation arises from "steric factors" and "sensitive districts" in the molecule is one which we had developed independently from our studies of the temperature dependence of ionic reactions, considered from the standpoint of the orientation theory.[21]

We can also support Scheffer and Brandsma's conclusion that the effect of a catalyst does not always result in a lowering of the energy of activation, by the following example. The velocity of the sodium bromoacetate-sodium thiosulfate reaction in highly dilute solution is increased over sixfold by the addition of small amounts of lanthanum chloride.[22]

For the range 0–25°C, it has been found that $E_{act.}$[23] *increases* from 15,850±64 to 17,700±55 calories by the addition of 0.03M $LaCl_3$. An increase of 1850 calories in $E_{act.}$ should of itself decrease the velocity, were it not more than counterbalanced by an increase in the entropy of activation as exhibited by an increase in *B* from 11.20 to 13.40. As was anticipated quite different results, are found for the β-bromopropionate-thiosulfate reaction.

The author wishes to acknowledge the constructive criticisms which he has received in the preparation of this paper from his colleagues and from Professor Otto Halpern of the Department of Physics of New York University.

VII. Conclusions

(1) Evidence is presented that the energy of activation, measured by the temperature coefficient of the reaction velocity, varies with temper-

[19] Scheffer and Brandsma, Rec. Trav. Chim. **45**, 522 (1926).

[20] Brandsma, ibid. **47**, 94 (1928); **48**, 1205 (1929).

[21] Reference 3, p. 2850; reference 4, p. 210.

[22] La Mer and Fessenden, J. Am. Chem. Soc. **54**, 2351 (1932).

[23] Unpublished work of La Mer and Kamner.

ature. This necessitates a consideration of the activation quantities, heat capacity, free energy and entropy.

(2) The kinetic character of these quantities becomes evident when they are developed from R. C. Tolman's statistical formulation of the Arrhenius equation.

(3) The Brönsted equation follows readily from the concept of free energy of activation. However, the development shows that the activity coefficient of the critical complex $f_{X(\text{act.})}$ is in general a kinetic quantity which becomes equivalent to the corresponding thermodynamic quantity only when all quantum levels have the same reactivity constant, or when only one quantum level is involved.

(4) A positive heat capacity of activation furnishes evidence that the critical state is multiple in the quantum sense and that it is illegitimate to replace $f_{X(\text{act.})}$ by a thermodynamic expression.

(5) The Hinshelwood-Moelwyn-Hughes collision theory can be valid only when the entropy of activation is zero, which is improbable from the standpoint of quantum theory, the thermodynamic requirements of equilibrium processes, or the available data for activation energies in the ranges of experimental measurement.

Evaluation of the Series Which Arise in the Calculation of Thermodynamic Quantities From Spectroscopic Data

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In cases where knowledge of the molecular spectrum of a gas is sufficiently detailed to include the "stretching" and "interaction" terms in the expression for the rotational-vibrational energy states, calculation of the free energy, entropy and heat capacity for high temperatures becomes very laborious when the usual approximations are employed. In this paper, methods are developed which reduce many such calculations to a matter of interpolation in appended tables; for cases which lie outside the range of the tables, approximations are given which materially reduce the labor of computation. The procedure is illustrated by calculations for chlorine, bromine, hydrogen chloride, carbon monoxide, oxygen and nitric oxide.

THE calculation of thermodynamic quantities (heat capacities, entropies and "free energies") from spectroscopic data is now a familiar process and provides an easy and accurate method of predicting chemical equilibria. In carrying out such calculations for diatomic molecules, one of two alternative procedures has in general been adopted. The first of these consists in computing the "state sum" and its derivatives from the empirically determined energy levels as presented in Eq. (3) below, the contribution of each rotational-vibrational state being calculated and the separate contributions added to form the sum. This method was first used by Hicks and Mitchell,[1] and has been extensively employed by Giauque and his associates.[2] It possesses the immense advantage of avoiding all assumptions as to the distribution of the levels, but becomes impossibly laborious if certain of the spectroscopic constants are small or the temperature is high. The second procedure is to treat the rotational-vibrational levels as those of a rigid rotator combined with those of either a harmonic or anharmonic oscillator, i.e., the terms involving D and F in Eq. (3) are ignored and the constant B is assumed to be independent of the vibrational quantum number. With these simplifying assumptions the rotational and vibrational parts of the state sum can be treated separately and the summation over the rotational levels can be replaced by a simple integration.

Giauque and Overstreet[3] seem to have been the first to recognize the need for an approximation which would take into account the second order "stretching" and "interaction" terms and would at the same time avoid the summation over all values of J. In the case of chlorine (a typical $^1\Sigma$ molecule) they deduced an expression which replaced by an integral the summation over the rotational levels in the state sum for a given vibrational state, and showed that the approximation was permissible whenever term-by-term summation was not feasible (see Eq. (4) below). Their method, however, becomes rather laborious if many vibrational states must be taken into account—either because the temperature is high or because the fundamental frequency of the molecule is small; moreover, if in addition to the free energy, the entropy and heat capacity are desired, not only must the state sum be computed but also its first and second derivatives with respect to temperature, and the calculation may then become very laborious.

In the present paper we describe methods which are applicable not only to $^1\Sigma$ but to $^3\Sigma$ and to $^2\Pi$ molecules, and which in many calculations eliminate the need for summation entirely; even for cases where these methods are not immediately applicable, approximations are developed which materially reduce the labor of

[1] Hicks and Mitchell, J. Am. Chem. Soc. **48**, 1520 (1926).

[2] For example—Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

[3] Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).

computation. One great advantage possessed by the procedure outlined below is that it permits an immediate estimate to be made of the uncertainty resulting in the calculated thermodynamic quantity from a given uncertainty in any of the spectroscopic constants, while a second desirable feature is the ease with which previously calculated numerical values can be revised in the light of new spectroscopic data. The methods are illustrated by calculations for various molecules, and since these examples are intended to show primarily the precision of the approximations, they are sometimes carried to a greater number of significant figures than is justified by the accuracy of the experimental data. With regard to the permissible error introduced by an approximation, it would seem that an accuracy of 0.0005 in the logarithm of the state sum (corresponding to an accuracy of one-twentieth of one percent in an equilibrium constant), of $0.001R$ in a molar entropy and of $0.005R$ in a molar heat capacity, would leave little to be desired by the physical chemist.

It may be noted in passing that while the discussion has been confined to diatomic molecules, the methods can be readily extended to corresponding calculations for the polyatomic case, and that the quantities tabulated at the end of this paper will be of use in such calculations whenever the spectroscopic data become available.

Calculation of the Free Energy

Giauque[4] has shown that if F is the free energy in calories at temperature T and pressure P atmospheres and E_0^0 is the additive energy constant at absolute zero, then

$$-(F-E_0^0)/RT=3/2\cdot\ln M+5/2\cdot\ln T-\ln P+\ln(2\pi k)^{3/2}/h^3N^{5/2}+\ln R'+\ln Q+E_0/RT, \quad (1)$$

where M is the molecular weight, k is the Boltzmann constant, N is the Avogadro number, h is Planck's constant, R is the gas constant in calories per degree, R' is the gas constant in cc-atmos. per degree, Q is the state sum defined by

$$Q=\sum_n p_n\cdot e^{-\epsilon_n/kT} \quad (2)$$

and E_0 is the energy in the lowest observable rotational-vibrational state. In Eq. (2), $\sum_n$ indicates summation over all rotational, vibrational and electronic levels which make appreciable contributions to the state sum, so that for moderate and high temperatures, at least a double summation is involved. For a heteronuclear $^1\Sigma$ molecule whose constituent atoms have no nuclear spin, $p_n=2J+1$ where J is the rotational quantum number and ϵ_n in cm^{-1} is given by

$$\epsilon_n=(v+\tfrac{1}{2})\omega_e-(v+\tfrac{1}{2})^2\omega_e x+B_v(J+\tfrac{1}{2})^2+D_v(J+\tfrac{1}{2})^4+F_v(J+\tfrac{1}{2})^6+\cdots, \quad (3)$$

where $B_v=B_0(1-\alpha v+\gamma v^2)$, etc., and v is the vibrational quantum number.

Giauque and Overstreet[3] have shown that for small values of B_vhc/kT the summation with regard to J for any given v may be replaced by an integration:

$$e^{E_0/RT}\cdot Q=e^{\epsilon_0hc/kT}\cdot\sum_v e^{-\epsilon_vhc/kT}\cdot e^{1/4q_0}\cdot Q_R \quad (4a)$$

$$=e^{\epsilon_0hc/kT}\cdot\sum_v e^{-\epsilon_vhc/kT}\cdot e^{1/4q_0}\cdot q_v(1+1/12q_v+d_v+3d_v^2+f_v+\cdots), \quad (4b)$$

where ϵ_v in $cm^{-1}=(v+1/2)\omega_e-(v+1/2)^2\omega_e x$, $q_v=kT/B_vhc$, $d_v=(-2D_v/B_v)q_v$, $f_v=(-6F_v/B_v)q_v^2$. It should be noted that Q_R is a function of v since q_v, d_v, and f_v are all functions of v. Indicating the ground vibrational state by the subscript zero, and setting $B_v=B_0/(1+\beta_1v+\beta_2v^2)$, the expression on the right of (4) may be replaced to a good approximation by

$$e^{\epsilon_0hc/kT}\cdot Q_V\cdot e^{1/4q_0}\cdot q_0(1+\beta_1\bar{v}+\beta_2\overline{v^2})(1+1/12q_0+d_0+3d_0^2+f_0), \quad (5)$$

where

$$Q_V=\sum_v e^{-\epsilon_vhc/kT},\quad \bar{v}=(\sum_v v\cdot e^{-\epsilon_vhc/kT})/Q_V,\quad \overline{v^2}=(\sum_v v^2\cdot e^{-\epsilon_vhc/kT})/Q_V.$$

[4] Giauque, J. Am. Chem. Soc. **52**, 4808 (1930).

The errors introduced by taking d and f for the ground vibrational state are usually negligible but a correction can be made if necessary as explained below. Hence to a sufficiently good approximation (since $1/12q_0, d_0, f_0, \beta_1\bar{v}$, etc., are all small compared with unity)

$$\ln Q+E_0/RT\approx(\ln Q_V+\epsilon_0hc/kT)+1/4q_0 +\ln q_0+\beta_1\bar{v}+\beta_2\overline{v^2}+1/12q_0+d_0+5d_0^2/2+f_0. \quad (6)$$

Of the quantities on the right of (6), q_0, β_1, β_2, d_0 and f_0 are known at once, while $(\ln Q_V+\epsilon_0hc/kT)$, $\bar{v}$ and $\overline{v^2}$ are functions only of $hc\omega_e/kT$ and of x; hence double-entry tables of these three quantities as functions of $w=hc\omega_e/kT$ and x lead at once to an approximate value of $(\ln Q+E_0/RT)$.

It should be noted that if the molecule is homonuclear, a symmetry correction $-\ln 2$ must be added to the right of Eqs. (4) and (6), while for each atom possessing a nuclear spin of j_s units, a spin correction $\ln(2j_s+1)$ must be added to the right of the same equations.[5]

Calculation of the Entropy and Heat Capacity

The entropy of a gas for temperature T and pressure P atmospheres is computed as the sum of the translational entropy S_T and of the rotational-vibrational entropy S_{RV}, where

$$S_T/R=3/2\cdot\ln M+5/2\cdot\ln T-\ln P +\ln(2\pi k/h^2)^{3/2}\cdot(e/N)^{5/2}+\ln R', \quad (7)$$

$$S_{RV}/R=\ln Q+T\partial\ln Q/\partial T, \quad (8)$$

and Q is defined in Eq. (4). From Eqs. (8) and (6), the approximate value of the rotational vibrational entropy is given by

$$S_{RV}/R\approx S_V/R+1+\ln q_0+\beta_1s_1+\beta_2s_2+2d_0 +15d_0^2/2+3f_0, \quad (9)$$

where

$$S_V/R=\ln Q_V+T\partial\ln Q_V/\partial T,$$

$$s_1=\bar{v}+T\partial\bar{v}/\partial T, \quad s_2=\overline{v^2}+T\partial\overline{v^2}/\partial T.$$

Where necessary, the same symmetry and spin corrections must be added to the right of (8) and (9) as to right of (4) and (6).

The heat capacity is given by $C_P=5R/2+C_{RV}$ where

$$C_{RV}=T\partial S_{RV}/\partial T \quad (10)$$

(see Eqs. (4) and (8)), while from Eqs. (9) and (10) the approximate value of the rotational vibrational heat capacity is given by

$$C_{RV}/R\approx C_V/R+1+\beta_1c_1+\beta_2c_2+2d_0 +15d_0^2+6f_0 \quad (11)$$

where

$$C_V/R=T\partial(S_V/R)/\partial T,$$

$$c_1=T\partial s_1/\partial T, \quad c_2=T\partial s_2/\partial T.$$

All of the nine quantities $(\ln Q_V+\epsilon_0hc/kT)$, S_V/R, C_V/R, $\bar{v}$, $\overline{v^2}$, s_1, s_2, c_1, c_2 have been tabulated as functions of x and $w=hc\omega_e/kT$ in Tables I–XI for $x\leqq0.02$ and $w\geqq0.6$. For $(\ln Q_V+\epsilon_0hc/kT)$, S_V/R, and C_V/R the value in each case must be obtained from two tables; first the value of the quantity in question for the given w and for $x=0$ must be found from Table I, and then the difference (for the given w) for $x=0$ and $x=x$ must be found from Tables II, III or IV as the case may be; this arrangement was adopted to facilitate interpolation. In the case of Tables I–VIII the interval is sufficiently fine to permit interpolation (involving not more than second differences) to yield results exact to a unit or so in the last place as printed; in the case of Tables IX–XI, all that is needed is a rough graphical interpolation. Tables II–IV only extend to $w=6$; the reason for this is that for $w>6$ an anharmonic

[5] These corrections are only approximate, but are valid whenever Bhc/kT is so small that Eqs. (4) and (6) are valid for the corresponding heteronuclear nonspinning case. As an example, consider a rigid homonuclear $^1\Sigma$ molecule with $j_s=\frac{1}{2}$, so that the symmetry and spin correction to the logarithm of the state sum is $-\ln 2+2\ln 2$. Assume that the weights (as in hydrogen) are $(2J+1)$ for J even and $3(2J+1)$ for J odd. The state sum is then

$$\sum_{J=0,2,\cdots}(2J+1)\cdot e^{-J(J+1)/q}+3\cdot\sum_{J=1,3,\cdots}(2J+1)\cdot e^{-J(J+1)/q} \quad (A)$$

Mulholland (Camb. Phil. Soc. Proc. **24**, 280, 1928), has shown that

$$\sum_{J=0,1,\cdots}(2J+1)\cdot e^{-J(J+1)/q}\approx e^{1/4q}\cdot q\cdot(1+1/12q+7/480q^2),$$

while from the known properties of the theta-functions

$$\sum_{J=0,1,\cdots}(-1)^J\cdot(2J+1)\cdot e^{-J(J+1)/q}\approx e^{1/4q}\cdot(\pi q)^{\frac{1}{2}}\cdot e^{-\pi^2q/4}.$$

Hence (A) may be replaced by

$$(4/2)\cdot e^{1/4q}\cdot q(1+1/12q+7/480q^2)-e^{1/4q}\cdot(\pi q)^{\frac{1}{2}}\cdot e^{-\pi^2q/4}. \quad (B)$$

For the term $7/480q^2$ to be <0.0001, q must be >12.5, a requirement which makes the last term in (B) negligible.

TABLE I. $w=hc\omega_e/kT$, $x=0$.

w	$(\ln Q_V+\epsilon_0 hc/kT)$	S_V/R	C_V/R	w	$(\ln Q_V+\epsilon_0 hc/kT)$	S_V/R	C_V/R
0.55	0.8603	1.6103	0.9752	2.6	0.0772	0.2858	0.5859
.60	.7959	1.5257	.9705	2.7	.0696	.2641	.5631
.65	.7382	1.4482	.9655	2.8	.0627	.2440	.5405
.70	.6863	1.3769	.9602	2.9	.0566	.2255	.5182
.75	.6394	1.3108	.9544	3.0	.0511	.2083	.4963
.80	.5966	1.2494	.9483	3.1	.0461	.1923	.4747
.85	.5576	1.1921	.9419	3.2	.0416	.1776	.4536
.90	.5218	1.1384	.9351	3.3	.0376	.1640	.4330
0.95	.4890	1.0881	.9281	3.4	.0339	.1513	.4129
1.00	.4587	1.0407	.9207	3.5	.0307	.1396	.3933
1.05	.4307	0.9959	.9130	3.6	.0277	.1288	.3743
1.10	.4048	.9536	.9050	3.7	.0250	.1188	.3558
1.15	.3807	.9136	.8967	3.8	.0226	.1096	.3380
1.20	.3584	.8756	.8882	3.9	.0205	.1010	.3207
1.25	.3376	.8395	.8794	4.0	.0185	.0931	.3041
1.30	.3182	.8052	.8703	4.2	.0151	.0791	.2726
1.35	.3001	.7725	.8610	4.4	.0124	.0670	.2436
1.40	.2832	.7414	.8515	4.6	.0101	.0568	.2170
1.45	.2673	.7117	.8418	4.8	.0083	.0481	.1928
1.50	.2525	.6833	.8319	5.0	.0068	.0407	.1708
1.55	.2386	.6562	.8217	5.2	.0055	.0344	.1508
1.60	.2255	.6303	.8114	5.4	.0045	.0290	.1329
1.65	.2132	.6055	.8010	5.6	.0037	.0245	.1168
1.70	.2017	.5817	.7904	5.8	.0030	.0207	.1025
1.75	.1909	.5590	.7796	6.0	.0025	.0174	.0897
1.80	.1807	.5371	.7687	6.4	.0016	.0123	.0682
1.85	.1711	.5162	.7577	6.8	.0011	.0087	.0516
1.90	.1620	.4962	.7466	7.2	.0007	.0061	.0387
1.95	.1535	.4769	.7354	7.6	.0005	.0043	.0289
2.00	.1454	.4584	.7241	8.0	.0003	.0030	.0215
2.1	.1306	.4236	.7013	8.4	.0002	.0021	.0159
2.2	.1174	.3916	.6783	8.8	.0002	.0015	.0117
2.3	.1056	.3620	.6552	9.2	.0001	.0010	.0086
2.4	.0951	.3346	.6320	9.6	.0001	.0007	.0062
2.5	.0857	.3092	.6089	10.0	.0000	.0005	.0045

oscillator defined by ω_e and x can be treated without sensible error as a harmonic oscillator of frequency $\omega_e(1-2x)$; for the same reason Tables V–VII only extend to $w=4$, for $w>4$ Table VIII being used. In all cases entries in the tables were computed by term-by term summation of the series involved up to the series limit (e.g., $v=24$ for $x=0.02$). For values of $w<0.6$, interpolation becomes in general impracticable, but for any isolated calculations in this range, special approximations are available (see Example 4 below).

The general method of using the tables can perhaps be best illustrated by a numerical example. Assume a heteronuclear $^1\Sigma$ molecule with nonspinning nuclei, whose energy levels are given by Eq. (3) and for which $w=hc\omega_e/kT=1.0$, $x=0.02$, $q_0=kT/B_0hc=3000$, $B_v=B_0(1-0.015v)$, $D_v=-10^{-6}B_v$. Then from Tables I and II, $(\ln Q_V+\epsilon_0 hc/kT)=0.4587+0.0422$; $\ln q_0=8.0064$, $1/4q_0=0.0001$, $\beta_1=0.015$, $\beta_2=2.25\times10^{-4}$, $d_0=0.0060$. From Table V $\bar{v}=0.687$, and from Table IX, $\overline{v^2}=1.79$. Hence

$$\ln Q+E_0/RT=0.4587+0.0422+0.0001+8.0064$$
$$+0.0103+0.0004+0.0060+0.0001=8.5242.$$

The exact value found from Eq. (4) by summation up to the series limit $v=24$ is 8.5242. To compute the entropy, $S_V/R=1.0407+0.0975$ (Tables I and III); $s_1=1.861$ (Table VI); $s_2=6.96$ (Table X); hence

$$S_{RV}/R=1.0407+0.0975+1+8.0064+0.0279$$
$$+0.0016+0.0120+0.0003=10.1864.$$

The exact value (Eqs. (4) and (8)) is 10.1865. To compute the heat capacity, $C_V/R=0.9207$

TABLE II. $(ln\ Q_v+\epsilon_0 hc/kT)_{w,x}-(ln\ Q_v+\epsilon_0 hc/kT)_{w,0}$ *as a function of* $w=hc\omega_e/kT$ *and* x.

w	$x=0.005$	0.010	0.015	0.020	0.025
0.6	0.0169	0.0358	0.0576	0.0837	0.1133
0.7	.0143	.0299	.0474	.0677	.0913
0.8	.0123	.0255	.0401	.0566	.0755
0.9	.0107	.0222	.0347	.0485	.0640
1.0	.0095	.0196	.0304	.0422	.0553
1.1	.0084	.0174	.0269	.0372	.0485
1.2	.0076	.0156	.0241	.0332	.0430
1.3	.0069	.0141	.0217	.0298	.0385
1.4	.0062	.0127	.0196	.0269	.0346
1.5	.0057	.0116	.0178	.0244	.0314
1.6	.0052	.0106	.0163	.0222	.0285
1.7	.0048	.0097	.0149	.0203	.0260
1.8	.0044	.0089	.0136	.0186	.0238
1.9	.0040	.0082	.0125	.0171	.0219
2.0	.0037	.0075	.0115	.0157	.0201
2.2	.0031	.0064	.0098	.0134	.0171
2.4	.0027	.0055	.0084	.0114	.0145
2.6	.0023	.0047	.0072	.0098	.0124
2.8	.0020	.0040	.0061	.0084	.0107
3.0	.0017	.0034	.0053	.0072	.0092
3.2	.0014	.0030	.0045	.0062	.0079
3.4	.0012	.0025	.0039	.0053	.0068
3.6	.0011	.0022	.0033	.0045	.0058
3.8	.0009	.0019	.0028	.0039	.0050
4.0	.0008	.0016	.0024	.0033	.0043
4.2	.0007	.0014	.0021	.0029	.0037
4.4	.0006	.0012	.0018	.0024	.0031
4.6	.0005	.0010	.0015	.0021	.0027
4.8	.0004	.0009	.0013	.0018	.0023
5.0	.0004	.0007	.0011	.0015	.0020
5.2	.0003	.0006	.0010	.0013	.0017
5.4	.0003	.0005	.0008	.0011	.0014
5.6	.0002	.0004	.0007	.0009	.0012
5.8	.0002	.0004	.0006	.0008	.0010
6.0	0.0002	0.0003	0.0005	0.0007	0.0009

TABLE III. $(S_v/R)_{w,x}-(S_v/R)_{w,0}$ *as a function of* $w=hc\omega_e/kT$ *and* x.

w	$x=0.005$	0.010	0.015	0.020	0.025
0.6	0.0357	0.0778	0.1317	0.2000	0.2695
0.7	.0302	.0649	.1069	.1598	.2206
0.8	.0263	.0557	.0899	.1318	.1822
0.9	.0232	.0488	.0777	.1124	.1534
1.0	.0207	.0434	.0685	.0975	.1318
1.1	.0187	.0390	.0613	.0863	.1153
1.2	.0171	.0355	.0554	.0775	.1026
1.3	.0157	.0325	.0505	.0703	.0923
1.4	.0145	.0299	.0464	.0643	.0840
1.5	.0135	.0277	.0428	.0592	.0770
1.6	.0125	.0258	.0397	.0548	.0710
1.7	.0117	.0241	.0370	.0509	.0658
1.8	.0110	.0225	.0347	.0475	.0612
1.9	.0103	.0211	.0325	.0445	.0572
2.0	.0097	.0199	.0305	.0417	.0536
2.2	.0086	.0177	.0270	.0369	.0473
2.4	.0077	.0158	.0241	.0329	.0420
2.6	.0069	.0141	.0216	.0294	.0376
2.8	.0062	.0127	.0194	.0263	.0336
3.0	.0056	.0114	.0174	.0236	.0301
3.2	.0050	.0102	.0156	.0212	.0270
3.4	.0045	.0092	.0140	.0190	.0242
3.6	.0040	.0082	.0125	.0170	.0217
3.8	.0036	.0073	.0112	.0152	.0194
4.0	.0032	.0066	.0100	.0136	.0174
4.2	.0029	.0059	.0090	.0122	.0155
4.4	.0025	.0052	.0080	.0108	.0138
4.6	.0022	.0046	.0071	.0096	.0123
4.8	.0020	.0041	.0063	.0085	.0109
5.0	.0018	.0036	.0055	.0076	.0097
5.2	.0016	.0032	.0049	.0067	.0086
5.4	.0014	.0028	.0043	.0059	.0076
5.6	.0012	.0025	.0038	.0052	.0067
5.8	.0011	.0022	.0033	.0046	.0059
6.0	0.0009	0.0019	0.0029	0.0040	0.0052

$+0.1263$ (Tables I and IV); $c_1=2.935$ (Table VII); $c_2=21.0$ (Table XI); hence

$$C_V/R=0.9207+0.1263+1+0.0440+0.0047$$
$$+0.0120+0.0005=2.108.$$

The exact value Eqs. (4), (8) and (10) is 2.109.

In general, the approximations grow worse the smaller w, the larger x, the larger β and the larger d. For large enough values of d, the error introduced by neglecting its variation with v may become appreciable; a partial correction may be made for this, however, by setting $d_v=d_0(1+\delta v)$ and then replacing the d_0 of (6), (9) and (11) by $\bar{d}=d_0(1+\delta\bar{v})$. For example, if the constants are those just given except that $D_v=-3\times10^{-6}B_v$, then $d_0=0.0180$ and $\bar{d}=0.0180(1+0.015\times0.687)=0.01818$; if $\bar{d}$ be used in Eqs. (6), (9) and (11), the approximate values are 8.5371, 10.2129 and 2.137 as compared with the exact values 8.5371, 10.2131 and 2.139, while if d_0 is used in the same equations, the approximate values are 8.5369, 10.2125 and 2.137 (see Examples 2 and 4).

Example 1*: $Cl_{35}-Cl_{35}$ at 1000°K

The constants[6] are $\omega_e=564.9$, $\omega_e x=4.0$, $B_v=0.24295-0.00170v$, $D_v=-1.830\times10^{-7}-3.1$

* In none of the examples has the nuclear spin correction been added, in Example 1 this would amount to 2 ln 6, and in example 2, to ln 12.

[6] Elliott, Proc. Roy. Soc. **A127**, 638 (1930) as quoted by Giauque and Overstreet, reference 3.

TABLE IV. $(C_v/R)_{w,x}-(C_v/R)_{w,0}$ *as a function of* $w=hc\omega_e/kT$ *and* x.

w	$x=0.005$	0.010	0.015	0.020	0.025
0.6	0.0384	0.0936	0.1852	0.2868	0.3213
0.7	.0324	.0752	.1416	.2331	.3058
0.8	.0278	.0631	.1128	.1863	.2658
0.9	.0244	.0544	.0940	.1515	.2235
1.0	.0219	.0480	.0809	.1263	.1871
1.1	.0198	.0430	.0713	.1083	.1585
1.2	.0182	.0391	.0639	.0950	.1364
1.3	.0168	.0358	.0580	.0850	.1195
1.4	.0157	.0332	.0533	.0772	.1068
1.5	.0147	.0310	.0494	.0708	.0969
1.6	.0139	.0292	.0462	.0658	.0888
1.7	.0132	.0276	.0435	.0615	.0822
1.8	.0126	.0262	.0412	.0579	.0770
1.9	.0121	.0251	.0392	.0549	.0726
2.0	.0116	.0241	.0376	.0523	.0691
2.2	.0110	.0224	.0348	.0481	.0628
2.4	.0104	.0211	.0326	.0449	.0582
2.6	.0098	.0200	.0309	.0424	.0547
2.8	.0094	.0192	.0294	.0403	.0517
3.0	.0090	.0184	.0282	.0384	.0492
3.2	.0087	.0177	.0271	.0368	.0470
3.4	.0084	.0170	.0260	.0353	.0450
3.6	.0080	.0163	.0249	.0338	.0430
3.8	.0077	.0156	.0238	.0323	.0411
4.0	.0073	.0149	.0227	.0308	.0392
4.2	.0070	.0142	.0216	.0293	.0372
4.4	.0066	.0135	.0205	.0278	.0353
4.6	.0063	.0127	.0194	.0262	.0333
4.8	.0059	.0120	.0182	.0247	.0314
5.0	.0055	.0112	.0171	.0231	.0294
5.2	.0051	.0104	.0159	.0216	.0275
5.4	.0048	.0097	.0148	.0201	.0256
5.6	.0044	.0090	.0137	.0186	.0237
5.8	.0041	.0083	.0127	.0172	.0219
6.0	0.0037	0.0076	0.0116	0.0158	0.0202

TABLE V. $\bar{v}$ *as a function of* $w=hc\omega_e/kT$ *and* x.

w	$x=0.00$	0.005	0.01	0.015	0.02
0.6	1.216	1.279	1.353	1.461	1.611
.7	0.986	1.031	1.083	1.152	1.248
.8	.816	0.849	0.888	0.936	0.999
0.9	.685	.711	.741	.776	.821
1.0	.582	.603	.627	.654	.687
1.1	.499	.516	.536	.557	.583
1.2	.431	.445	.461	.479	.499
1.3	.375	.386	.400	.415	.432
1.4	.327	.338	.349	.362	.375
1.5	.287	.296	.306	.317	.328
1.6	.253	.261	.269	.279	.289
1.7	.224	.231	.238	.246	.255
1.8	.198	.204	.211	.218	.225
1.9	.176	.181	.187	.193	.200
2.0	.157	.162	.167	.172	.178
2.2	.125	.128	.133	.137	.142
2.4	.100	.103	.107	.110	.114
2.6	.080	.083	.086	.089	.092
2.8	.065	.067	.069	.072	.074
3.0	.053	.054	.056	.058	.060
3.2	.043	.044	.046	.048	.049
3.4	.035	.036	.037	.039	.040
3.6	.028	.029	.030	.032	.033
3.8	.023	.024	.025	.026	.027
4.0	0.019	0.020	0.020	0.021	0.022

$\times 10^{-9}v$, $F=-9.4\times10^{-14}$. Hence,[7] $w=0.80905$, $x=0.00708$, $q_0=2873.9$, $1/4q_0=0.00009$, $\beta_1=0.0070$, $\beta_2=4.9\times10^{-5}$, $d_0=0.00433$, $f_0=0.00002$. Then $(\ln Q_v+\epsilon_0hc/kT)=0.5893+0.0174$ (Tables I and II); $\bar{v}=0.850$ (Table V); $\overline{v^2}=2.3_5$ (Table IX). Since the molecule is homonuclear, the symmetry correction is $-\ln 2=-0.69315$; hence the approximate value of $(\ln Q+E_0/RT)$ by Eq. (6) is 7.8875 while the exact value (Eq. (4)) is 7.8876. Similarly, $S_V/R=1.2387+0.0376$ (Tables I and III); $s_1=2.121$ (Table VI); $s_2=8.1_5$ (Table X). Hence, including the symmetry correction, $S_{RV}/R=9.5707$ (exact value by Eq. (8), 9.5709). From Tables I and IV, $C_V/R=0.9472+0.0393$, $c_1=2.78$ (Table VII); $c_2=19._6$ (Table XI). Hence C_{RV}/R by Eq. (11) is 2.016 while the exact value by Eq. (10) is 2.017.

[7] In this as in the other examples hc/k was taken to be 1.43221.

Example 2: HCl_{35} at 3000°K

The constants[8] are $\omega_e=2994.33$, $\omega_ex=53.58$, $B_v=10.4469-0.3161v+0.01195v^2$, $D_v=-0.000527+0.000012v$, $F=1.46\times10^{-8}$. Hence $w=1.42950$, $x=0.01789$, $q_0=200.50$, $\beta_1=0.03026$, $\beta_2=-0.000228$, $\bar{d}=0.02023(1+0.0377\bar{v})=0.02050$, $f_0=-0.00034$. From the tables $(\ln Q_V+\epsilon_0hc/kT)=0.2736+0.0231$, $S_V/R=0.7236+0.0553$, $C_V/R=0.8458+0.0649$, $\bar{v}=0.355$, $\overline{v^2}=0.64$, $s_1=1.036$, $s_2=2.4_0$, $c_1=1.670$, $c_2=6._5$. Eqs. (6), (9) and (11) give 5.6310, 7.1536, and 2.005 as the values of $(\ln Q+E_0/RT)$, S_{RV}/R and C_{RV}/R, respectively, while the exact values (Eqs. (4), (8) and (10)) are 5.6310, 7.1535 and 2.005.

Example 3: CO at 3000°K

The constants[9] are $\omega_e=2167.4$, $\omega_ex=12.70$, $B_v=1.843-0.020v$, $D_v=-5.453\times10^{-6}-6.9\times10^{-8}v$. Hence, $w=1.0347$, $x=0.00586$, $q_0=1136.5$, β_1

[8] Kemble, J. Opt. Soc. Am. **12**, 1 (1926).

[9] Snow and Rideal, Proc. Roy. Soc. **A125**, 462 (1929), as quoted by Clayton and Giauque, J. Am. Chem. Soc. **54**, 2610 (1932).

TABLE VI. s_1 *as a function of* $w=hc\omega_e/kT$ *and* x.

w	$x=0.000$	0.005	0.010	0.015	0.020
0.6	2.834	3.023	3.283	3.706	4.280
.7	2.358	2.494	2.670	2.930	3.318
.8	2.001	2.104	2.231	2.403	2.661
0.9	1.724	1.804	1.901	2.024	2.201
1.0	1.503	1.567	1.643	1.736	1.861
1.1	1.322	1.375	1.436	1.509	1.602
1.2	1.171	1.216	1.266	1.325	1.397
1.3	1.044	1.081	1.124	1.173	1.230
1.4	0.936	0.968	1.004	1.045	1.092
1.5	.842	.870	0.901	0.936	0.975
1.6	.760	.785	.812	.842	.876
1.7	.688	.711	.734	.760	.789
1.8	.625	.645	.666	.689	.714
1.9	.569	.586	.605	.625	.648
2.0	.519	.534	.551	.569	.589
2.2	.433	.446	.459	.474	.490
2.4	.363	.374	.385	.398	.411
2.6	.306	.315	.324	.334	.345
2.8	.258	.266	.274	.283	.292
3.0	.218	.225	.231	.239	.247
3.2	.184	.190	.196	.203	.210
3.4	.156	.161	.166	.172	.178
3.6	.132	.137	.141	.146	.151
3.8	.112	.116	.120	.124	.129
4.0	0.095	0.098	0.102	0.106	0.110

TABLE VII. c_1 *as a function of* $w=hc\omega_e/kT$ *and* x.

w	$x=0.000$	0.005	0.010	0.015	0.020
0.6	3.332	3.734	4.426	5.791	6.966
.7	2.854	3.142	3.577	4.396	5.512
.8	2.496	2.712	3.013	3.526	4.355
0.9	2.217	2.384	2.606	2.947	3.528
1.0	1.992	2.126	2.297	2.540	2.935
1.1	1.808	1.918	2.054	2.236	2.515
1.2	1.654	1.745	1.856	1.999	2.203
1.3	1.522	1.599	1.692	1.807	1.963
1.4	1.409	1.475	1.553	1.647	1.771
1.5	1.310	1.367	1.433	1.512	1.613
1.6	1.222	1.272	1.330	1.397	1.481
1.7	1.144	1.188	1.238	1.297	1.367
1.8	1.073	1.112	1.157	1.208	1.269
1.9	1.009	1.044	1.084	1.129	1.184
2.0	0.951	0.982	1.018	1.058	1.104
2.2	.847	.874	0.902	0.934	0.970
2.4	.758	.780	.804	.831	.861
2.6	.680	.699	.719	.742	.766
2.8	.611	.627	.645	.664	.685
3.0	.548	.563	.578	.595	.613
3.2	.492	.505	.519	.534	.550
3.4	.441	.453	.466	.478	.493
3.6	.395	.406	.417	.429	.442
3.8	.353	.363	.373	.384	.396
4.0	0.316	0.324	0.334	0.343	0.354

TABLE VIII. $w=hc\omega/kT$, $x=0$.

w	4.4	4.8	5.2	5.6	6.0	6.4	6.8	7.2	7.6	8.0
$\bar{v}$	0.012	.008	.006	.004	.002	.002	.001	.001	.001	.000
s_1	0.068	.048	.035	.025	.017	.012	.009	.006	.004	.003
c_1	0.250	.196	.153	.118	.090	.069	.052	.039	.029	.022

TABLE IX. $\overline{v^2}$ *as a function of* $w=hc\omega_e/kT$ *and* x.

w	$x=0.000$	0.005	0.010	0.015	0.020
0.6	4.18	4.66	5.34	6.58	8.44
0.7	2.93	3.22	3.61	4.22	5.23
0.8	2.15	2.33	2.57	2.92	3.47
0.9	1.62	1.75	1.91	2.12	2.44
1.0	1.26	1.35	1.46	1.60	1.79
1.2	0.80	0.85	0.91	0.98	1.07
1.4	.53	.57	.61	.65	0.69
1.6	.38	.40	.42	.45	.48
1.8	.28	.29	.30	.32	.34
2.0	.21	.22	.23	.24	.25
2.4	.12	.12	.13	.14	.14
2.8	.07	.07	.08	.08	.09
3.2	0.05	0.05	0.05	0.05	0.05

TABLE X. s_2 *as a function of* $w=hc\omega_e/kT$ *and* x.

w	$x=0.000$	0.005	0.010	0.015	0.020
0.6	13.66	15.70	19.03	25.86	34.43
0.7	9.71	10.94	12.75	16.10	21.44
0.8	7.20	8.00	9.08	10.88	13.99
0.9	5.51	6.05	6.76	7.82	9.64
1.0	4.32	4.71	5.20	5.87	6.96
1.2	2.82	3.03	3.29	3.62	4.07
1.4	1.94	2.08	2.23	2.42	2.65
1.6	1.40	1.49	1.58	1.69	1.83
1.8	1.04	1.10	1.16	1.24	1.33
2.0	0.80	0.83	0.87	0.92	0.99
2.4	.49	.51	.54	.56	.59
2.8	.32	.33	.35	.36	.38
3.2	0.21	0.22	0.23	0.24	0.25

$=0.0109$, $\beta_2=1.2\times10^{-4}$, $d_0=0.00673$. From the tables, $(\ln Q_V+\epsilon_0 hc/kT)=0.4390+0.0107$, $S_V/R=1.0092+0.0237$, $C_V/R=0.9154+0.0251$, $\bar{v}=0.573$, $\overline{v^2}=1.26$, $s_1=1.508$, $s_2=4.40$, $c_1=2.072$, $c_2=10.8$. Eqs. (6), (9) and (11) give 7.4989, 9.0994 and 1.979 as the approximate values of

TABLE XI. *c_2 as a function of $w=hc\omega_e/kT$ and x.*

w	$x=$ 0.000	0.005	0.010	0.015	0.020
0.6	30.0	36.7	50.6	80.8	101.3
0.7	21.6	25.6	32.6	48.4	70.0
0.8	16.3	18.9	22.8	31.1	44.8
0.9	12.6	14.4	16.9	21.5	30.2
1.0	10.0	11.3	13.0	15.8	21.0
1.2	6.7	7.4	8.3	9.5	11.6
1.4	4.7	5.2	5.7	6.3	7.3
1.6	3.5	3.8	4.1	4.5	5.0
1.8	2.7	2.9	3.1	3.3	3.7
2.0	2.1	2.2	2.4	2.5	2.8
2.4	1.3	1.4	1.5	1.6	1.7
2.8	0.9	1.0	1.0	1.1	1.1
3.2	0.7	0.7	0.7	0.8	0.8

(ln $Q+E_0/RT$), S_{RV}/R and C_{RV}/R, respectively, while the exact values (Eqs. (4), (8) and (10)) are 7.4991, 9.0997 and 1.980.

Example 4: $Br_{79}-Br_{81}$ at 1500°K

The constants[10] are $\omega_e=323.2$, $\omega_e x=1.07$, $B_v=0.08077-0.000275v$, $D=-2.03\times10^{-8}$. Hence $w=0.3086$, $x=0.00331$, $q_0=12966.8$, $\beta_1=0.003405$, $\beta_2=1.16\times10^{-5}$, $\bar{d}=d_0(1+\delta\bar{v})=0.00651(1+0.00681\bar{v})$. With this value of w, the tables are of course inapplicable; but the series necessary to evaluate the quantities involved in Eqs. (6), (9) and (11) can be computed without inordinate labor by means of the integral approximations listed below.

The general method is to compute the first few terms of the series in question and then replace the remaining terms by an integral; the evaluation of $\exp[\epsilon_0 hc/kT]\cdot Q_V$ may serve as an example. The values of $\exp[(\epsilon_0-\epsilon_v)hc/kT]=\exp[-v(1-x)w+v^2wx]$ for $v=1, 2, \cdots 10$ are computed and added, the result being 3.69403. The remaining terms from 11 up are summed by the well-known relation

$$\sum_{v=M}^{N} f(v)=\int_M^N f(y)\cdot dy+(1/2)[f(N)+f(M)]+(1/12)[\Delta_{N-1}'-\Delta_M']+(1/24)[\Delta_{N-2}''+\Delta_M'']+(19/720)[\Delta_{N-3}'''-\Delta_M''']+(3/160)[\Delta_{N-4}^{IV}+\Delta_M^{IV}]+\cdots, \quad (12)$$

where

$$\Delta_R'=f(R+1)-f(R),\quad \Delta_R''=\Delta_{R+1}'-\Delta_R',$$
$$\Delta_R'''=\Delta_{R+1}''-\Delta_R'',\quad \Delta_R^{IV}=\Delta_{R+1}'''-\Delta_R'''\quad \text{etc.}$$

and N is the series limit. Here

$$\int_M^N f(y)\cdot dy=\int_M^N \exp[-y(1-x)w+y^2wx]\cdot dy$$
$$=(1/r)\cdot\{\exp[-2Mrs+M^2r^2]\cdot F(s-Mr)-\exp[-2Nrs+N^2r^2]\cdot F(s-Nr)\}, \quad (13)$$

where

$$2rs=(1-x)w,\quad r^2=wx,$$
$$F(\alpha)=\exp[-\alpha^2]\cdot\int_0^\alpha \exp[y^2]\cdot dy,$$

a quantity already tabulated by Lash Miller and Gordon.[11] Thus by computing $f(v)$ for $v=M$, $M+1$, $M+2$, $M+3$ and for $v=N-3$, $N-2$, $N-1$, N (which is sufficient to evaluate the difference terms in Eq. (12)), it is possible to obtain a numerical value for the sum of the remaining terms in the series.

In the case of bromine, $N\approx150$, and for 1500°K, terms depending on N are negligible; $r=0.0319604$, $s=4.81187$; for $M=11$, $s-Mr=4.46031$, $F(4.46031)=0.115163$, $2Mrs-M^2r^2=3.25980$. Hence the expression on the right of (13) $=0.13835$ and the sum of the terms from $v=11$ to the series limit is 0.15847; therefore $\exp[\epsilon_0 hc/kT]\cdot Q_V=3.69403+0.15847=3.8525$; the value found by term-by-term summation up to $v=50$ is 3.85258.

The series involved in S_V/R, C_V/R, $\bar{v}$, $\overline{v^2}$, s_1, s_2, c_1, and c_2 can be evaluated similarly by means of Eq. (12), the requisite integrals being as follows Writing $\int$ for the integral from M to N, E, E_M and E_N for $2rsy-r^2y^2$, $2Mrs-M^2r^2$, and $2Nrs-N^2r^2$, and $[E]$, $[E_M]$, and $[E_N]$ for $\exp[-E]$ $\exp[-E_M]$, and $\exp[-E_N]$,

$$I_1=\int[E]\cdot dy=(1/r)\cdot\{[E_M]\cdot F(s-Mr)-[E_N]\cdot F(s-Nr)\}, \quad (14)$$
$$I_2=\int E\cdot[E]\cdot dy=(s^2+\tfrac{1}{2})\cdot I_1-(\tfrac{1}{2}r)\cdot\{(s-Mr)\cdot[E_M]-(s-Nr)\cdot[E_N]\},$$

[10] Brown, Phys. Rev. **39**, 777 (1932).
[11] Lash Miller and Gordon, J. Phys. Chem. **35**, 2878–2882 (1931).

$$I_3 = \int E^2 \cdot [E] \cdot dy = -s^2 \cdot I_1 + (s^2 + \tfrac{3}{2}) \cdot I_2 - (1/2r) \cdot \{(s - Mr) \cdot E_M \cdot [E_M] - (s - Nr) \cdot E_N \cdot [E_N]\},$$

$$I_4 = \int y \cdot [E] \cdot dy = (s/r) \cdot I_1 - (1/2r^2) \cdot \{[E_M] - [E_N]\},$$

$$I_5 = \int y \cdot E \cdot [E] \cdot dy = (s/r) \cdot I_2 - (1/2r^2) \cdot \{(E_M + 1) \cdot [E_M] - (E_N + 1) \cdot [E_N]\},$$

$$I_6 = \int y \cdot E^2 \cdot [E] \cdot dy = (s/r) \cdot I_3 - (1/2r^2) \cdot \{(E_M^2 + 2E_M + 2) \cdot [E_M] - (E_N^2 + 2E_N + 2) \cdot [E_N]\},$$

$$I_7 = \int y^2 \cdot [E] \cdot dy = (2s/r) \cdot I_4 - I_2/r^2,$$

$$I_8 = \int y^2 \cdot E \cdot [E] \cdot dy = (2s/r) \cdot I_5 - I_3/r^2,$$

$$I_9 = \int y^2 \cdot E^2 \cdot [E] \cdot dy = (2s/r) \cdot I_6 - (1/r^2) \cdot \{s^2 \cdot I_1 - 3(s^2 + \tfrac{1}{2}) \cdot I_2 + (s^2 + \tfrac{7}{2}) \cdot I_3 - (\overline{s - Mr}/2r) \cdot E_M \cdot (E_M - 1) \cdot [E_M] + (\overline{s - Nr}/2r) \cdot E_N (E_N - 1) \cdot [E_N]\},$$

$$F(\alpha) = e^{-\alpha^2} \cdot \int_0^\alpha e^{y^2} \cdot dy.$$

With the aid of the recursion formulae listed above, all the integrals necessary for the calculation can be readily computed once I_1 has been found; to preserve numerical accuracy in the higher integrals, it is advisable to compute I_1 to two or three decimal places more than are needed for the calculation of $\exp[\epsilon_0 hc/kT] \cdot Q_V$.

These approximations give $(\ln Q_V + \epsilon_0 hc/kT) = 1.3487$, $S_V/R = 2.2267$, $C_V/R = 1.0438$, $\bar{v} = 2.923$, $\overline{v^2} = 20.6$, $s_1 = 6.48$, $s_2 = 68$, $c_1 = 7.58$, $c_2 = 1.6 \times 10^2$; $\bar{d} = 0.00664$, $\ln q_0 = 9.4701$. Therefore, $(\ln Q + E_0/RT) = 10.8358$, $S_{RV}/R = 12.7333$ and $C_{RV}/R = 2.085$; the exact values (Eqs. (4), (8) and (10)) are 10.8358, 12.7335 and 2.086. The surprisingly good agreement in this case in spite of the small value of w is due to the fact that x, β and d are also small.

Example 5: $O_{16} - O_{16}$ at 3000°K

The normal electronic state of the oxygen molecule is $^3\Sigma$ so that the rotational levels fall into closely spaced triplets designated by Mulliken[12] F_1, F_2 and F_3. The weight factors are $p_J = 2J+1 = 2K+3, 2K+1, 2K-1$ for F_1, F_2 and F_3 respectively where K designates the number of units of rotational angular momentum. Let ϵ^+ denote $F_1(K) - F_2(K)$ and ϵ^-, $F_3(K) - F_2(K)$; both ϵ^+ and ϵ^- vary somewhat with K but without serious error may be taken as constant. Let the index $+$ denote constants for F_1 and $-$ constants for F_3, constants for F_2 being without index, and for convenience let the zero of energy be the state $v = 0$, $K = 1$ for F_2. From the known properties of the theta-functions

$$2\sum \exp[-(K+1/2)^2 B_v hc/kT - (K+1/2)^4 \cdot D_v hc/kT] \approx (\pi q_v)^{\frac{1}{2}}(1 + 3d_v/8), \quad (15)$$

where $q_v = kT/B_v hc$ and $D_v = (-2D_v/B_v)q_v$. Therefore, since the molecule is homonuclear

$$e^{E_0/RT} \cdot Q = \tfrac{1}{2}\sum_v e^{(\epsilon_0 - \epsilon_v)hc/kT} \cdot e^{9/4q_0} \times [e^{-\epsilon^+ hc/kT} \cdot \{Q_R^+ + (\pi q_v^+)^{\frac{1}{2}}(1 + 3d_v^+/8)\} + Q_R + e^{-\epsilon^- hc/kT} \cdot \{Q_R^- - (\pi q_v^-)^{\frac{1}{2}}(1 + 3d_v^-/8)\}] \quad (16)$$

where Q_R is defined in Eq. (4). Hence to a good approximation

$$\ln Q + E_0/RT \approx -\ln 2 + (6) + 2/q_0 + \ln \Delta, \quad (17)$$

$$S_{RV}/R \approx -\ln 2 + (9) + s_\Delta, \quad (18)$$

$$C_{RV}/R \approx (11) + c_\Delta, \quad (19)$$

where (6), (9) and (11) indicate the expressions on the right of these three equations with the values of q_0, β_1, β_2, and d_0 or $\bar{d}$ for F_2, and Δ, s_Δ and c_Δ are defined by

$$\Delta = (q_0^+/q_0) \cdot (1 + (\pi/q_0^+)^{\frac{1}{2}}) \cdot e^{-\epsilon^+ hc/kT} + 1 + (q_0^-/q_0) \cdot (1 - (\pi/q_0^-)^{\frac{1}{2}}) \cdot e^{-\epsilon^- hc/kT},$$

$$s_\Delta = \ln \Delta + T\partial \ln \Delta/\partial T, \quad (20)$$

$$c_\Delta = T\partial s_\Delta/\partial T.$$

The term $2/q_0 (= 9/4q_0 - 1/4q_0)$ in Eq. (17) arises from the fact that the lowest rotational vibrational state has $J = 1$, i.e., $K = 1$ for F_2 while the term $-\ln 2$ in Eqs. (17) and (18) is the symmetry correction for a homonuclear molecule.

[12] Mulliken, Phys. Rev. **32**, 880 (1928).

The constants[13] are $\omega_e = 1576.78$, $\omega_e x = 11.37$, $B_v^+ = B_v = B_v^- = 1.4375(1-0.0111v)$, $D_v^+ = D_v = D_v^- = 3.32\times10^{-6}B_v$, $\epsilon^+ = -2.11$, $\epsilon^- = -1.90$. Hence $w = 0.75276$, $x = 0.00721$, $q_0 = 1457.15$, $\beta_1 = 0.0111$, $\beta_2 = 1.23\times10^{-4}$, $\bar{d} = 0.00968(1+0.0111\bar{v}) = 0.00978$. From the tables $(\ln Q_V + \epsilon_0 hc/kT) = 0.6369 + 0.0193$, $S_V/R = 1.3073 + 0.0415$, $C_V/R = 0.9541 + 0.0452$, $\bar{v} = 0.947$, $\overline{v^2} = 2.84$, $s_1 = 2.335$, $s_2 = 9.7_7$, $c_1 = 3.035$, $c_2 = 23._6$. In the case of oxygen, however, there is another complication due to the fact that the first excited electronic level, which is $^1\Sigma$, is only 13,123 cm^{-1} above the normal level. Hence for this temperature, it is necessary to add to the expression on the right of (16) one-half the product of the expression on the right of Eq. (4) into $\exp[-A_0hc/kT]$ where $A_0 = 13{,}123$, the rotational and vibrational constants for (4) being those for the first excited level, viz., $\omega_e' = 1426.9$, $\omega_e'x' = 11.9$, $B' = 1.3912$.

To a first approximation, the contribution from the $^1\Sigma$ state may be allowed for in Eqs. (17), (18) and (19) by adding a term $\exp[-A_0hc/kT]$ to the expression for Δ on the right of (20). This of course ignores the change in the rotational-vibrational constants in the excited state as compared with the normal. If Q_V' denote the value of Q_V for $w = 1426.9hc/kT = 0.6812$ and $x = 0.00834$, this variation can be taken into account by adding to the right of (17), (18) and (19) respectively

$$r\cdot e^{-A_0hc/kT}, \quad r(A_0hc/kT)\cdot e^{-A_0hc/kT}, \quad r(A_0hc/kT)^2\cdot e^{-A_0hc/kT}, \tag{21}$$

where $r = \{(Q_V' - Q_V)/Q_V + (B_0 - B')/B'\}/3$. Since $(\ln Q_V' + \epsilon_0' hc/kT)$ for $w = 0.6812$ and $x = 0.00834$ is 0.7305 while $(\ln Q_V + \epsilon_0 hc/kT)$ is 0.6562, the correcting terms (21) are 0.00007, 0.0004 and 0.0028 respectively.

Including the contributions from the $^1\Sigma$ state, $\ln \Delta = 1.09988$, $s_\Delta = 1.10321$ and $c_\Delta = 0.0248$; taking account of the corrections (21), Eqs. (17), (18) and (19) give 8.3697, 10.0909 and 2.084 as the approximate values of $(\ln Q + E_0/RT)$, S_{RV}/R and C_{RV}/R, while the exact values (Eq. (16)) are 8.3699, 10.0911 and 2.085 respectively.[14]

Example 6: NO at 3000°K

In a $^2\Pi$ molecule such as nitric oxide, the rotational levels fall into two groups, $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, the energy levels being given by

$$\begin{aligned}\epsilon = \epsilon_V + \epsilon_r &= (v+1/2)\omega_e - (v+1/2)^2\omega_e x \\ &+ A(J+1/2) + B_v(J+1/2)^2 \\ &+ C(J+1/2)^3 + D(J+1/2)^4,\end{aligned} \tag{22}$$

where $B_v = B_0(1-\alpha v+\gamma v^2) = B_0/(1+\beta_1 v+\beta_2 v^2)$ and $J = 1/2, 3/2, 5/2\cdots$ for $^2\Pi_{1/2}$, $J = 3/2, 5/2\cdots$ for $^2\Pi_{3/2}$. The weight factors (excluding nuclear spin weight) are $2(2J+1)$, the factor 2 arising from the Λ-type doubling of the rotational levels. The terms involving A and C as determined by Jenkins, Barton and Mulliken[15] are of much less importance than the D term, so that

$$\begin{aligned}p\cdot\exp[-\epsilon_r hc/kT] \approx 2(2J+1)\cdot\exp[-(J+\tfrac{1}{2})^2 B_v hc/kT]\cdot\{1-(J+\tfrac{1}{2})\cdot Ahc/kT \\ -(J+\tfrac{1}{2})^3\cdot Chc/kT - (J+\tfrac{1}{2})^4\cdot Dhc/kT + (J+\tfrac{1}{2})^8\cdot(Dhc/kT)^2/1\cdot2\}.\end{aligned} \tag{23}$$

For summation over all positive integral values of n

$$\sum 2n\cdot e^{-n^2b} \approx 1/b - 1/6, \quad \sum 2n^2\cdot e^{-n^2b} \approx (1/2b)\cdot(\pi/b)^{\frac{1}{2}}. \tag{24}$$

Hence, if constants for $^2\Pi_{1/2}$ be indicated by $+$, and those for $^2\Pi_{3/2}$ by $-$,

$$e^{E_0/RT}\cdot Q = 2e^{-\epsilon_0 hc/kT}\cdot e^{1/q_0}[\sum e^{-\epsilon_v^+ hc/kT}\cdot Q_R^+ + e^{-\epsilon d hc/kT}\cdot\sum e^{-\epsilon_v^- hc/kT}\cdot\{Q_R^- - 2e^{-1/q_v^-}\}], \tag{25}$$

[13] Mecke and Wurms, Zeits. f. Physik **61**, 37 (1930). Mecke and Baumann, Zeits. f. Physik **73**, 139 (1931).

[14] By using the values of the constants as given in *International Critical Tables*, and by normalizing to the state $K = 1$ for F_3 (which involves adding $-2.13hc/kT$ to the right of Eq. (17)), the approximations for 3000°K give 59.459, 67.848 and 9.108 as the values of $(E_0^0 - F^0)/T$, S^0 and C_p^0 respectively. Johnston and Walker (J. Am. Chem. Soc. **55**, 187 (1933)) found 59.458, 67.848 and 9.108 by summation.

[15] Jenkins, Barton and Mulliken, Phys. Rev. **30**, 150 (1927).

where $Q_R=q_v(1-1/6q_v+a_v+c_v+d_v+3d_v^2)$, $q_v=kT/B_vhc$, $a_v=(-A/2B_v)\cdot(\pi/q_v)^{\frac{1}{2}}$, $c_v=(-3C/4B_v)\times(\pi q_v)^{\frac{1}{2}}$, $d_v=(-2D/B_v)\cdot q_v$ and ϵ_d is the doublet separation. If symbols without index denote the quantities obtained by averaging the corresponding quantities for $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ then to a good approximation

$$\ln Q+E_0/RT\approx\ln 2+(\ln Q_V+\epsilon_0hc/kT)+1/q_0^+ +\ln q_0+\beta_1\bar{v}+\beta_2\overline{v^2}$$
$$-1/6q_0+a_0+c_0+d_0+5d_0^2/2+\ln\Delta, \quad (26)$$

$$S_{RV}/R\approx\ln 2+S_V/R+1+\ln q_0+\beta_1s_1+\beta_2s_2+a_0/2+3c_0/2+2d_0+15d_0^2/2+s_\Delta, \quad (27)$$

$$C_{RV}/R\approx C_V/R+1+\beta_1c_1+\beta_2c_2-a_0/4+3c_0/4+2d_0+15d_0^2+c_\Delta, \quad (28)$$

where
$$\Delta=q_0^+/q_0+(q_0^-/q_0)\cdot\{1-(2/q_0)\cdot e^{-1/q_0^-}\}\cdot e^{-\epsilon_dhc/kT},$$
$$s_\Delta=\ln\Delta+T\partial\ln\Delta/\partial T, \quad (29)$$
$$c_\Delta=T\partial s_\Delta/\partial T,$$

and the quantities $\bar{v}$, $\overline{v^2}$, s_1, s_2, c_1, and c_2 are as defined under Eqs. (5), (9) and (11). If necessary, the d_0 of Eqs. (26), (27) and (28) may be replaced by $\bar{d}=d_0(1+\delta\bar{v})$.

The constants[15] are: for $^2\Pi_{1/2}$, $\omega_e=1906.54$, $\omega_ex=14.424$, $B_v=1.675-0.0178v$, $A=0.0071$, $C=0.000106$, $D=-5.06\times10^{-6}$; for $^2\Pi_{3/2}$, $\omega_e=1906.43$, $\omega_ex=14.454$, $B_v=1.724-0.0187v$, $A=0.0070$, $C=0.000010$, $D=-8.71\times10^{-6}$; $\epsilon_d=124.4$. Hence $w=0.91016$, $x=0.007574$, $q_0=(1250.53+1215.00)/2=1232.76$, $\beta_1=(0.01063+0.01085)/2=0.01074$, $\beta_2=1.14\times10^{-4}$, $a_0=-0.00010$, $c_0=-(0.00297+0.00027)/2=-0.00162$; $d_0=(0.00756+0.01228)/2=0.00992$ while $\bar{d}=0.00992(1+0.0215\bar{v})=0.01007$; $\ln\Delta=0.66354$, $s_\Delta=0.69269$, $c_\Delta=0.0009$. From the tables, $(\ln Q_V+\epsilon_0hc/kT)=0.5149+0.0163$, $S_V/R=1.1279+0.0356$, $C_V/R=0.9337+0.0385$, $\bar{v}=0.713$, $\overline{v^2}=1.7_8$, $s_1=1.823$, $s_2=6.2$, $c_1=2.456$, $c_2=15._1$. Eq. (26) gives 9.0220 as the value of $(\ln Q+E_0/RT)$, the exact value from Eq. (25) being 9.0221; similarly, Eqs. (27) and (28) give 10.0750 and 2.022 as the approximate values of S_{RV}/R and C_{RV}/R, while from (25), the exact values[16] are 10.7052 and 2.024.

Schmid, Koening and von Farkas[17] in their analysis of the rotational structure of the nitric oxide spectrum found $B_v=1.69-0.0175v$ for $^2\Pi_{1/2}$, $B_v=1.73-0.0190v$ for $^2\Pi_{3/2}$, $C=-0.0015$, $\epsilon_d=120$. If these values be used, higher terms in the expansion of exp $[-(J+1/2)^3\cdot Chc/kT]$ must be included and Q_R of Eq. (24) will become $q_v\cdot[1-1/6q_v+c_v+(16/3\pi)c_v^2+\cdots]$. The terms in a and d will be omitted from Eqs. (26), (27) and (28), and c_0 must be replaced by $\bar{c}=c_0(1+\delta\bar{v})$; moreover $(16/3\pi-1/2)\bar{c}^2$ must be added to right of (26) and $(32/3\pi-1)\bar{c}^2$ must be added to the right of (27) and (28). Here $q_0=(1239.44+1210.79)/2=1225.12$, $\beta_1=(0.01036+0.01098)/2=0.01067$, $\beta_2=1.14\times10^{-4}$, $c_0=(0.04154+0.04010)/2=0.04082$, $\bar{c}=0.04082(1+0.016\bar{v})=0.04129$, $\ln\Delta=0.66446$, $s_\Delta=0.69271$, $c_\Delta=0.0009$. Hence the approximate values of $(\ln Q+E_0/RT)$, S_{RV}/R and C_{RV}/R are 9.0514, 10.7463 and 2.036, while the exact values (Eq. (25)) are 9.0516, 10.7470 and 2.040.

[16] With the values of the universal constants as given in *International Critical Tables*, Eqs. (26), (27) and (28) lead to the results 60.566, 68.877 and 8.984 for $(E_0^0-F^0)/T$, S^0 and C_p^0 respectively. Johnston and Chapman (J. Am. Chem. Soc. **55**, 153 (1933)) find by summation for 3000°K 60.567, 68.877 and 8.982; for 75°K, the approximations give 32.747, 40.029 and 7.806, as compared with their 32.747, 40.028 and 7.806.

[17] Schmid, Koenig and von Farkas, Zeits. f. Physik **64**, 84 (1930).

The Free Energy of Steam and of Carbon Dioxide

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The free energy of steam is computed from the moments of inertia determined by Mecke and Baumann, and from the fundamental frequencies of Mecke and of Plyler, for temperatures up to 3000°K. From these numbers, the free energy of carbon dioxide (computed from Martin and Barker's data), the known free energies of carbon monoxide and hydrogen, and the thermal data of Rossini, the equilibrium constant for the water-gas reaction is obtained. The calculated equilibrium constants agree with the best experimental values for the temperature range 700°–1259°K within the limits of error of the experiments. The equilibrium constant for the dissociation of steam into diatomic oxygen and hydrogen is also tabulated, but an unambiguous comparison with experiment is not possible for this reaction, since steam may also dissociate into hydroxyl and hydrogen and the data necessary for a reliable calculation of the hydroxyl dissociation are not available. A calculation for the producer-gas equilibrium predicts greater dissociation of the CO_2 into CO and graphite than is found by experiment; this discrepancy can be accounted for if graphite is assumed to have a "zero point" entropy in excess of that given by the third law of thermodynamics.

IN a recent paper[1] the equilibrium constant for the water-gas reaction $CO+H_2O=CO_2+H_2$ was calculated from spectroscopic data. In that calculation, Mecke's older values[2] for the moments of inertia of the water molecule (0.98, 1.80, 2.80×10^{-40}) were used and the resulting $R\ln K$ were in general about 0.2 calory per degree less than the experimental values of Neumann and Koehler.[3] Since that time, two independent determinations of the rotational constants have appeared, the first by Lueg and Hedfeld[4] and the second by Mecke and Baumann,[5] and as a result a more accurate calculation is now possible for reactions involving steam.

Lueg and Hedfeld give for the moments of inertia $A=0.97$, $B=2.13$, $C=3.07\times10^{-40}$, while Mecke and Baumann give $A=1.09$, $B=1.907$, $C=2.985\times10^{-40}$. In the calculation of the "free energy" and entropy for moderate and high temperatures, it is the effective moment of inertia $\bar{I}=(ABC)^{\frac{1}{3}}$ which is the significant quantity, and either set of rotational constants leads to approximately the same result. In the following calculations, the values used were $B=1.907\times10^{-40}$, $C=2.985\times10^{-40}$, $A=C-B=1.078\times10^{-40}$, giving $\bar{I}=1.831\times10^{-40}$; had Lueg and Hedfeld's moments of inertia been selected, $\bar{I}$ would have been 1.851×10^{-40}, and the entropy and $-(F^0-E_0^0)/T$ (Table I) would have been 0.033 greater throughout.

As far as the vibrational contributions to the entropy and free energy are concerned, there is still an uncertainty as to the third fundamental frequency of the water molecule. Mecke[6] gives $\delta=1600$, $\nu(\pi)=3740$, $\nu(\sigma)=3850$ cm^{-1}; while Plyler[7] gives $\delta=1597$, $\nu(\pi)=3742$, $\nu(\sigma)=5309$ cm^{-1}. For any temperature less than 1000°K, either assignment leads to the same value of $-(F^0-E_0^0)/T$ within 0.01 cal./deg.; for temperatures greater than 1000°, however, the contribution of $\nu(\sigma)$ becomes appreciable, and for this reason $-(F^0-E_0^0)/T$ in the range 1100°–3000° has been computed both for Plyler's and Mecke's frequencies, the values based on the latter being indicated by the star.

The free energy is obtained from the familiar relation

$$-(F^0-E_0^0)T = -7.267+5R/2\cdot\ln T+3R/2\cdot\ln 18.016 +3R/2\cdot\ln 8\pi^{7/3}\bar{I}kT/h^2-R\cdot\ln 2+R\cdot\ln Q_r,$$

[1] Gordon and Barnes, J. Phys. Chem. **36**, 1143 (1932).
[2] Mecke, Trans. Faraday Soc. **26**, 214 (1930).
[3] Neumann and Koehler, Zeits. f. Elektrochemie **34**, 218 (1928).
[4] Lueg and Hedfeld, Zeits. f. Physik **75**, 512 (1932).
[5] Mecke and Baumann, Phys. Zeits. **33**, 833 (1932).
[6] Mecke, Zeits. f. Physik **64**, 173 (1930).
[7] Plyler, Phys. Rev. **39**, 77 (1932).

TABLE I. *The free energy of steam.*

$T°K$	298.1	300	400	500	600	700
$-(F^0-E_0^0)/T$	37.226	37.28	39.57	41.36	42.83	44.09
$T°K$	800	900	1000	1100	1200	1300
$-(F^0-E_0^0)/T$	45.19	46.18	47.07	47.88	48.64	49.34
			47.07*	47.89*	48.66*	49.36*
$T°K$	1400	1500	1600	1800	2000	2200
$-(F^0-E_0^0)/T$	50.00	50.62	51.21	52.30	53.30	54.22
	50.03*	50.66*	51.26*	52.37*	53.38*	54.33*
$T°K$	2400	2600	2800	3000		
$-(F^0-E_0^0)/T$	55.08	55.88	56.64	57.35		
	55.20*	56.02*	56.80*	57.53*		

* The starred entries in Table I are computed from Mecke's fundamental frequencies, unstarred from those of Plyler.

in which $\bar{I}=1.831\times10^{-40}$, $-R\ln 2$ is the Ehrenfest symmetry correction, and Q_v stands for the product of the state sums for three harmonic oscillators corresponding to the three fundamental modes of vibration of the molecule. The resulting values[8] of $-(F^0-E_0^0)/T$ are given in Table I. The nuclear spin contribution of the two hydrogen atoms ($2R\ln 2=2.754$) has not been included and must be added to the entries if they are to be used in conjunction with Giauque's table for hydrogen.[9] The entropy follows at once from the relation $S^0=-\partial F^0/\partial T$; for 298.1° (including the vibrational entropy 0.008, and the nuclear spin entropy 2.754) it is 47.93 cal./deg. In spite of the uncertainty as to the change in the spectroscopic constants in the higher rotational-vibrational states, the entries in Table I are probably accurate to two or three hundredth's of a calorie per degree up to 1000°, with a considerably larger uncertainty at the highest temperatures.

Of the other gases involved in the water-gas reaction, the free energies of hydrogen[9] and carbon monoxide[10] are known, and an approximate calculation for carbon dioxide can be made from the data of Martin and Barker[11]; they give $I=70.8\times10^{-40}$, $\delta=667.5$, $\nu(s)=1286$, $\nu(a)=2350$ cm^{-1}, the deformation frequency δ being doubly degenerate. There is an additional complication due to the interaction of $\nu(s)$ with δ which tends to remove the degeneracy of some of the δ levels. The error introduced by neglecting this interaction, even at 1500°K, is not serious, and for lower temperatures is quite negligible. In computing the entries of Table II, this interaction was therefore ignored, but a rough idea of the

TABLE II. *The free energy of carbon dioxide.*

$T°K$	298.1	300	400	500	600	700	800
$-(F^0-E_0^0)/T$	43.575	43.62	45.85	47.69	49.28	50.68	51.94
$T°K$	900	1000	1100	1200	1300	1400	1500
$-(F^0-E_0^0)/T$	53.10	54.16	55.15	56.08	56.95	57.77	58.54

error introduced thereby can be obtained from considering the interaction of the levels $n_\delta=2$, $n_s=0$, $n_a=0$ and $n_\delta=0$, $n_s=1$, $n_a=0$. Ignoring the interaction, the contribution to the vibrational state sum is that of three coincident levels of energy $2\times667.5=1335$ cm^{-1} and a single level of energy 1286 cm^{-1}. In reality, there are four distinct nondegenerate levels[12] of energy 1286, 1316, 1340 and 1388 cm^{-1}; as far as the calculation of $-(F^0-E_0^0)/T$ for 1500° is concerned, however, the use of the actual energy values for these two quantum states would only change the entry in Table II by 0.003 cal./deg. The values of $-(F^0-E_0^0)/T$, computed in the usual way, are given in Table II for temperatures up to

[8] In the calculations, the values of the universal constants are those given in *International Critical Tables*, Vol. I.

[9] Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

[10] Clayton and Giauque, J. Am. Chem. Soc. **54**, 2610 (1932).

[11] Martin and Barker, Phys. Rev. **41**, 291 (1932).

[12] Badger and Sho-Chow Woo, J. Am. Chem. Soc. **54**, 3523 (1932).

1500°K, the corresponding entropy for 298.1° being 51.09. The numbers, even for the highest temperature of the table, are probably reliable to a few units in the second decimal place.

The Water-Gas Equilibrium

From Rossini's values for the heats of combustion of hydrogen[13] and carbon monoxide[14] (68,313 and 67,623 cals., respectively) and Osborne, Stimson and Fiock's value[15] for the latent heat of vaporization of water (2439 joules per gram = 10,504 cal. per mole at 25°C), ΔH_{298} for the reaction $CO+H_2O=CO_2+H_2$ is -9814 cal. Since the entropies of hydrogen[9] and carbon monoxide[10] are 33.98 and 47.31 for 298.1°, $\Delta S_{298.1^0}=-10.17$, and therefore $\Delta F_{298.1^0}$ is -6782 cal. From Tables I and II and the values of $-(F^0-E_0^0)/T$ at 298.1° for carbon monoxide and hydrogen, $\Delta E_0^0=-9636$ cal. The resulting $R \ln K = R \ln p_{CO} \cdot p_{H_2O}/p_{CO_2} \cdot p_{H_2}$ for the range 600°–1500° are given in Table III; in arriving at these values, entries in Table I based on Plyler's frequencies were used.

Table III. *The equilibrium constant for the water-gas reaction.*

$K = p_{CO} \cdot p_{H_2O}/p_{CO_2} \cdot p_{H_2}$.

T°K	600	700	800	900	1000
$-R \ln K$	6.49	4.32	2.74	1.54	0.62
T°K	1100	1200	1300	1400	1500
$-R \ln K$	−0.11	−0.70	−1.18	−1.58	−1.91

Neumann and Koehler[3] found as the mean of a large number of measurements at 1259°, $K=1.61$, i.e., $R \ln K=0.947$; the value interpolated from Table II for this temperature is 1.00, i.e., $K=1.65$. With four exceptions, their results for 700° to 1259° give $R \ln K$ which lie within ± 0.12 cal./deg. of the numbers obtained from Table III. For the range 1100°–1259° (measurements at seven different temperatures) the mean deviation of the experimental $R \ln K$ from the calculated is -0.05; for the range 900°–1100° (measurements at eight temperatures) the mean deviation is -0.04; and for the range 700°–900° (measurements at five temperatures) the mean deviation is $+0.06$.

Emmett and Schultz[16] obtained values of the equilibrium constant for this reaction from their data on the reduction of cobalt oxide by carbon monoxide and by hydrogen. The values of $R \ln K$ from their measurements at 723°, 788° and 843° are -3.95, -2.90 and -2.14, respectively, as compared with -3.91, -2.90 and -2.18 from Table III.

Giauque and Ashley[17] have shown that the spectroscopic data lead to a value for the free energy of formation of steam in agreement with the best measurements on the mercuric oxide equilibria, and also in agreement with some calculations of their own for the Deacon reaction. It has been shown here that the same data lead to an equilibrium constant for the water-gas reaction which agrees with the most careful measurements of that quantity within the limits of error of the experiments.

The Thermal Dissociation of Steam

From Johnston and Walker's value[18] for the entropy of oxygen at 298.1°, viz., 49.02, $\Delta S_{298.1^0}$ for the reaction $H_2+\frac{1}{2}O_2=H_2O(g)$ is -10.56; combining this with Rossini's value[13] for $\Delta H_{298.1}$ ($-57{,}809$ cal.), $\Delta F_{298.1^0}=-54{,}661$; therefore, from the known free energies of hydrogen[9] and oxygen,[18] $\Delta E_0^0=-57{,}121$. The resulting $R \ln K = R \ln (p_{H_2O})/(p_{H_2}) \cdot (p_{O_2})^{\frac{1}{2}}$ are given in Table IV for temperatures[19] from 1300° to 3000°. As in the

Table IV. *The equilibrium constant for the "oxygen" dissociation of steam.*

$K = (p_{H_2O})/(p_{H_2}) \cdot (p_{O_2})^{\frac{1}{2}}$.

T°K	1300	1400	1500	1600	1800	2000
$R \ln K$	32.33	29.05	26.18	23.67	19.48	16.12
T°K	2200	2400	2600	2800	3000	
$R \ln K$	13.36	11.05	9.07	7.38	5.90	

[13] Rossini, Bur. Standards J. Research **6**, 1 (1931).

[14] Rossini, Bur. Standards J. Research **6**, 37 (1931).

[15] Osborne, Stimson and Fiock, Bur. Standards J. Research **5**, 411 (1930).

[16] Emmett and Schultz, J. Am. Chem. Soc. **52**, 1782 (1930).

[17] Giauque and Ashley, Phys. Rev. **43**, 81 (1933). Their value of ΔF for steam is $-54{,}669$, while the value obtained here is $-54{,}661$. The slight discrepancy arises from the fact that they used 10,490 as the latent heat of vaporization and 47.92 as the entropy.

[18] Johnston and Walker, J. Am. Chem. Soc. **55**, 172 (1933).

[19] The oxygen numbers are subject to some uncertainty at the higher temperatures owing to the possible existence

case of the water-gas reaction, the numbers in Table I used in computing Table IV were those based on Plyler's frequencies.

A comparison of Table IV with the experimental data for the dissociation of steam is subject to some uncertainty. If the experimental results be accepted at their face value, the agreement between the $R \ln K$ obtained by various workers[20] for the temperature range 1300°–2200°K and the numbers obtained from Table IV is surprisingly close—in general within ±0.3 cal./deg. Such agreement must be to some extent fortuitous, however, since Bonhoeffer and Reichardt[21] have shown, qualitatively at any rate, that the "hydroxyl" equilibrium $H_2O = OH + \frac{1}{2}H_2$ is at least as important as the "oxygen" equilibrium computed in Table IV. Unfortunately a reliable calculation of the hydroxyl dissociation is not possible at present owing to the uncertainty as to the value of ΔE_0^0 for the reaction; until this point is settled, a comparison of the experimental results with Table IV is largely guess-work.

The Producer-Gas Equilibrium

From Rossini's[14] heat of combustion of carbon monoxide (67,623 cal.) and Roth and Naeser's heat of combustion of graphite[22] as corrected by Clayton and Giauque,[10] viz., 94,240 cal., $\Delta H_{298.1} = 41{,}006$ cal. for the reaction $C(\beta \text{ graphite}) + CO_2 = 2CO$. If the "third law" entropy of graphite (1.39 at 298.1°) be accepted, then $\Delta S_{298.1}^0 = 42.15$ and $\Delta F_{298.1}^0$ is 28,441 (corresponding to a free energy of formation for CO_2 at this temperature of −94,443 cal.) From Clayton and Giauque's tables for carbon monoxide and graphite, and Table II, $\Delta E_0^0 = 39{,}352$ cal.; the resulting $R \ln K = R \ln (p_{CO})^2/(p_{CO_2})$ are given in Table V for temperatures from 600° to 1500°K.

Table V. *The equilibrium constant for the producer-gas reaction.*

$K = (p_{CO})^2/(p_{CO_2})$.

T°K	600	700	800	900	1000
$R \ln K$	−25.91	−16.10	−8.77	−3.10	+1.42
T°K	1100	1200	1300	1400	1500
$R \ln K$	+5.09	+8.14	+10.69	+12.87	+14.75

The experimental $R \ln K$ for the temperature range 1073°–1473°, obtained from the measurements of Rhead and Wheeler,[23] of Jellinek and Diethelm,[24] of Dent and Cobb[25] and of Becker[26] are quite self-consistent but are uniformly about 0.5 cal./deg. less than the corresponding numbers obtained from Table V. Of the quantities used in computing the table, there is no reason to suspect the heats of combustion or the spectroscopic entropies and free energies of the oxides of carbon. The position is different with respect to the graphite numbers, since it is possible that there is a "zero-point" entropy not included in the extrapolated integration to absolute zero. If *ad hoc*, for the sake of argument, a zero point entropy of 0.5 cal./deg. be assumed for graphite, the entropy at 298.1° will be 1.89, and all the entries in Clayton and Giauque's table of $-(F^0 - E_0^0)/T$ will be increased by 0.5. $\Delta F_{298.1}^0$ for the producer-gas reaction will then be 28,590

a $^1\Delta$ level; see Lewis and von Elbe (J. Am. Chem. Soc. **55**, 511 (1933)). Such a level makes a contribution to $-(F^0 - E_0^0)/T$ of approximately $2R/3 \exp[-17{,}200/RT]$, i.e., Johnston and Walker's values of $-(F^0 - E_0^0)/T$ will be increased by 0.004 at 1500°K and by 0.074 at 3000°K; the corresponding $R \ln K$ will be decreased by one-half these amounts.

[20] Int. Crit. Tab., Vol. VII, p. 231.

[21] Bonhoeffer and Reichardt, Zeits. f. physik. Chemie **139**, 75 (1928). Bonhoeffer and Reichardt's calculation of $K_{OH} = (p_{H_2O})/(p_{H_2})^{\frac{1}{2}} \cdot (p_{OH})$ is in error, since they did not allow correctly for the multiplicity of the rotational levels of the hydroxyl molecule. By using the spectroscopic constants given by Weizel (*Bandenspektren*, Leipzig, p. 327 (1931)) the values of $-(F^0 - E_0^0)/T$ for hydroxyl are 48.35, 50.44, 52.11 and 53.50 for 1500°, 2000°, 2500° and 3000° respectively. The calculation is similar to that for NO discussed by Gordon and Barnes (J. Chem. Phys. **1**, 297 (1933)) except that the II-doublet is inverted, with the result that the lowest observable state has $v=0$, $J=3/2$ for $^2\Pi_{3/2}$; the numbers just given include the item $R \ln 2$ which allows for the Λ-type doubling of the rotational levels but do not include the spin contribution of the hydrogen atom. If Bonhoeffer and Reichardt's estimate $\Delta E_0^0 = -64$ Cal. for the reaction $\frac{1}{2}H_2 + OH = H_2O$ be accepted, then $R \ln K_{OH}$ for the four temperatures is 27.2, 16.0, 9.3 and 4.8 respectively. Since ΔE_0^0 is possibly in error by several kilo-calories, these $R \ln K_{OH}$ are uncertain to the extent of several calories per degree.

[22] Roth and Naeser, Zeits. f. Elektrochemie **31**, 461 (1925).

[23] Rhead and Wheeler, J. Chem. Soc. **99**, 1140 (1911).

[24] Jellinek and Diethelm, Zeits f. anorg. Chemie **124**, 203 (1922).

[25] Dent and Cobb, J. Chem. Soc. **1929**, p. 1903.

[26] Becker, J. Iron Steel Inst. (London) **121**, 337 (1930).

cal., all the $R \ln K$ in Table V will be decreased by 0.5 cal./deg., and the free energies of formation of the two oxides will be $-32{,}850$ cal. and $-94{,}290$ cal. for CO and CO_2, respectively. In a recent survey of this and other technical gas reactions, Chipman[27] gives 28,570 as the "best" experimental value of $\Delta F_{298.1}^0$ for the producer-gas reaction; the result obtained by assuming a zero point entropy for graphite of 0.5 cal./deg. is in very close agreement with his value.

A natural way to settle the question as to the proper value of the entropy of graphite would be to compute it from the entropy of carbon vapor, the vapor pressure of graphite, and the heat of sublimation. Unfortunately, the requisite experimental data[28] are not known with sufficient accuracy to permit such a calculation. The results for the producer-gas reaction suggest, however, that in other reactions involving graphite the possibility that the "third law" entropy is too small should be borne in mind.

[27] Chipman, Ind. Eng. Chem. **24**, 1013 (1932).

[28] See a recent paper by Vaughan and Kistiakowsky, Phys. Rev. **40**, 457 (1932).

Cross-Activation in the Unimolecular Decomposition of Mixtures of Gaseous Methyl and Ethyl Ether

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On account of the disagreement between previous investigations of Kassel and the writer, the decomposition of mixtures of methyl and ethyl ether has been reinvestigated with greater accuracy. The cross-activation efficiency has been found to be considerably greater than that previously reported. It is, however, decidedly smaller than that for collisions between molecules of the same kind.

INTRODUCTION

IN previous communications[1] it was reported that mixtures of gaseous methyl and ethyl ether decomposed at rates determined solely by the partial pressures of the two ethers, and hence the efficiency of energy transfer in cross collisions of the second kind was apparently zero. Kassel[2] repeated the work and found efficiencies between 66 and 153 percent, depending on the pressure. He therefore concluded that, while the actual values were somewhat uncertain, the cross-activation efficiency must be close to 100 percent.

The present paper describes a repetition of the work with considerably greater accuracy, in an attempt to settle the question of the discrepancy between the two investigations.

SOURCES OF ERROR

Variations in temperature are almost invariably the most important source of error in investigations of the kinetics of homogeneous gas reactions. This is especially true in the case of unimolecular reactions on account of their high temperature coefficients. In the case of the ether decompositions, the rates vary from 10 to 15 percent per degree difference in temperature.

In the previous investigations of Kassel and the writer ordinary electric furnaces were employed. In both cases the average temperature was probably constant to within about 0.5°C. This, however, is equivalent to about 6 to 7 percent error in the rates of reaction, and will largely mask the effect under investigation. Any attempt to obtain greater accuracy must therefore involve considerably better temperature control.

EXPERIMENTAL PROCEDURE

The reaction velocities were followed in the usual way by admitting the reactant or reactants to a heated silica bulb connected to a capillary manometer, and observing the change in pressure at regular intervals of time. Except for the temperature bath, the apparatus was identical with one which has been used in previous investigations.[3] The necessary temperatures were obtained by immersing the reaction bulb in a well-stirred bath of molten lead and tin (80 percent lead).

The bath consisted of a 12 inch length of 7 inch wrought iron pipe, to the bottom of which was welded a flat iron plate. It contained about 4 liters of molten metal. The iron pipe was covered with asbestos paper and wound with 16 gauge nichrome wire. The bath was packed in a steel container with fire-brick and loose asbestos. It was stirred vigorously by a wrought iron stirrer, the shaft of which passed through a small hole in the fire-brick lid.

Temperatures were measured with a chromel-alumel thermocouple in conjunction with a Cambridge thermocouple potentiometer which

[1] Steacie, J. Am. Chem. Soc. **54**, 1695 (1932); J. Phys. Chem. **36**, 1562 (1932).

[2] Kassel, J. Am. Chem. Soc. **54**, 3641 (1932). I am indebted to Dr. Kassel for communicating his results to me prior to their regular publication.

[3] Steacie, Can. J. Research **6**, 265 (1932).

could be read to about 0.05°C. The thermocouple was checked at the freezing and boiling points of water, and at the boiling point of sulphur.

Rough temperature control was effected by a 200 cc Pyrex bulb filled with air and immersed in the bath, and connected to a thermal regulator of the ordinary type. With this the temperature could be maintained constant to within about 2°C. During a run the temperature was controlled by hand regulation of rheostats.

On account of the high heat capacity of the contents of the bath, fluctuations in temperature were reduced to a minimum, while the high heat conductivity of the lead-tin mixture and the stirring ensured uniformity of temperature. The temperature could be maintained constant to at least 0.1°C. No variation in temperature throughout the bath could be detected.

The efficiency of the heat insulation is shown by the fact that a temperature of 478°C could be maintained by a power consumption of about 350 watts. On account of the efficient insulation, the bath was almost air-tight, and the lead-tin mixture did not oxidize to any great extent. After about two months continuous operation at 478°C, only about 5 percent of the lead-tin mixture had oxidized.

Methyl and ethyl ether were prepared and stored as previously described.

Experimental Results

The relative rates of reaction were inferred, as in Kassel's investigation, by comparing the fractional pressure increases at 5 minute intervals for 20 minutes in each run. For the first 5 minutes readings were taken at 1 minute intervals and extrapolated to zero time to give the initial pressure. Runs with the separate ethers and with the mixture were made in random order. The values of the fractional pressure increase in 20 minutes for various initial pressures are given in Tables I, II and III.

The data are plotted in Figs. 1, 2 and 3. In order to obtain lines of small curvature, the values of the fractional pressure increase are plotted against $\log_{10} P_0$ rather than against P_0 itself.

It was considered desirable to draw the curves through the experimental points by a computational method, so as to avoid any doubts as to the objectivity. The curves have therefore been drawn by fitting the experimental results to empirical equations of the type

$$\Delta P_{20}/P_0 = a + b \log P_0 + c(\log P_0)^2.$$

The fitting has been done by the method of averages, since the additional labor involved in the use of least squares did not seem to be warranted by the experimental accuracy.

Table I. *Fractional pressure increase in 20 minutes for ethyl ether at 478°C.*

P_0 cm	$\Delta P_{20}/P_0$	P_0 cm	$\Delta P_{20}/P_0$
35.40	0.2720	15.89	0.2128
35.34	0.2610	14.40	0.2143
34.45	0.2669	14.30	0.2080
33.92	0.2642	13.27	0.1989
31.49	0.2740	12.98	0.1918
29.95	0.2530	12.89	0.1850
28.93	0.2535	10.91	0.1803
26.65	0.2492	10.20	0.1843
24.76	0.2355	9.42	0.1632
23.38	0.2578	9.23	0.1700
22.90	0.2330	9.06	0.1622
22.25	0.2375	8.79	0.1801
20.94	0.2238	7.58	0.1660
20.53	0.2265	7.55	0.1629
18.76	0.2242	7.33	0.1498
18.38	0.2233	7.19	0.1680
17.74	0.2161	6.88	0.1584
17.63	0.2318	6.56	0.1645
17.10	0.2122	6.50	0.1493
16.42	0.2070	5.70	0.1486

Table II. *Fractional pressure increase in 20 minutes for methyl ether at 478°C.*

P_0 cm	$\Delta P_{20}/P_0$	P_0 cm	$\Delta P_{20}/P_0$
60.23	0.3250	15.46	0.1934
53.10	0.3130	14.52	0.1665
52.65	0.3120	13.68	0.1746
51.80	0.2938	13.37	0.1533
42.57	0.2800	11.37	0.1530
35.86	0.2510	10.89	0.1478
35.50	0.2644	9.84	0.1484
35.13	0.2570	9.54	0.1440
34.89	0.2455	8.86	0.1420
30.35	0.2542	8.51	0.1468
27.10	0.2250	7.82	0.1176
24.84	0.2136	7.48	0.1257
24.73	0.2262	6.97	0.1205
24.61	0.2180	6.95	0.1180
22.69	0.2019	6.74	0.1317
21.74	0.2150	6.19	0.1117
19.07	0.1892	6.09	0.1132
17.83	0.1926	5.41	0.1182
17.53	0.1778	4.14	0.1037
17.49	0.1987		

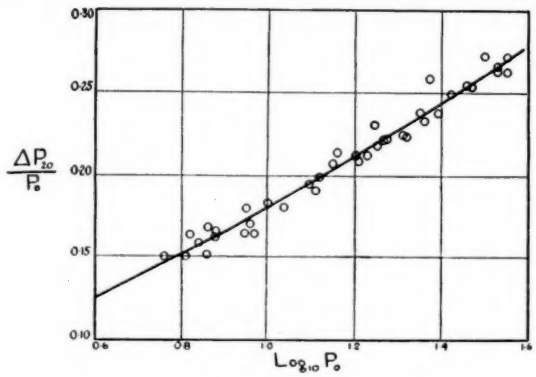

FIG. 1. Ethyl ether.

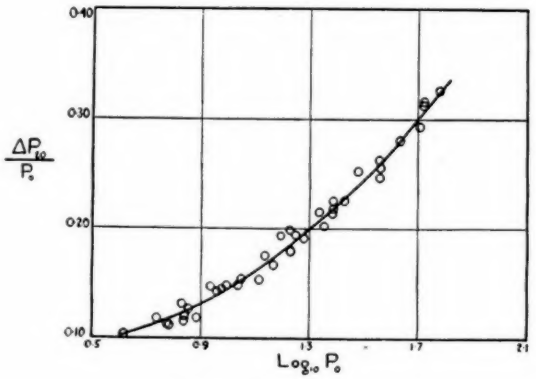

FIG. 2. Methyl ether.

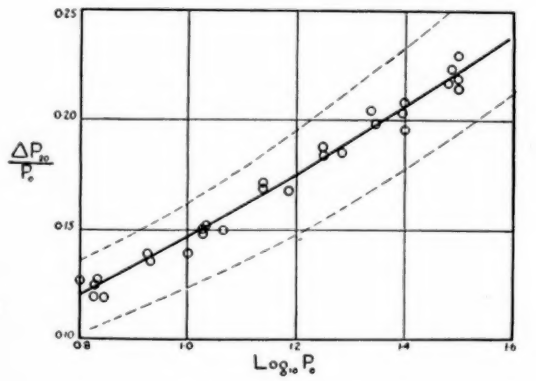

FIG. 3. 1 : 1 mixture.

The cross-activation efficiencies have been calculated by comparing the values of the fractional pressure increase in 20 minutes for the mixture with those calculated for the separate ethers: (A) on the assumption that each ether in the mixture will decompose at a rate determined by its *partial* pressure, i.e., on the assumption of zero efficiency of energy transfer between unlike molecules; and (B) assuming that the rate of decomposition of each ether in the mixture will correspond to its rate of decomposition when alone at a pressure equal to the *total* pressure of the mixture, i.e., assuming 100 percent efficiency of energy transfer between unlike molecules. The results are shown in Table IV.

Since complications may arise during the later stages of the reactions, it is obviously desirable to compare the relative rates of reaction at the earliest possible stage. Kassel accomplished this

TABLE III. *Fractional pressure increase in 20 minutes for a one to one mixture of ethyl and methyl ether at 478°C.*

P_0 cm	$\Delta P_{20}/P_0$	P_0 cm	$\Delta P_{20}/P_0$
31.87	0.2298	14.95	0.1657
31.78	0.2142	13.89	0.1722
31.65	0.2175	13.77	0.1700
31.07	0.2238	11.72	0.1500
30.48	0.2165	10.88	0.1517
25.12	0.2075	10.76	0.1525
24.98	0.1950	10.72	0.1485
24.87	0.2030	9.99	0.1391
22.07	0.1985	8.54	0.1356
21.63	0.2047	8.41	0.1390
19.51	0.1846	6.97	0.1190
17.70	0.1885	6.85	0.1284
17.53	0.1824	6.73	0.1248
15.61	0.1682	6.70	0.1193
15.26	0.1708	6.27	0.1275

TABLE IV. *Cross-activation efficiencies.*

P_0 cm	$\log_{10} P_0$	Fractional pressure increase in 20 minutes, observed: Ethyl ether	Methyl ether	Mixture	Fractional pressure increase calculated for mixture, assuming: 100 percent efficiency	Zero efficiency	Percent cross activation efficiency
4.0	0.60	0.125	0.101	0.095	0.113	——	——
5.0	0.70	0.137	0.109	0.107	0.123	——	——
6.3	0.80	0.151	0.119	0.120	0.135	——	——
7.9	0.90	0.165	0.131	0.133	0.148	0.113	57
10.0	1.00	0.180	0.145	0.146	0.163	0.123	58
12.6	1.10	0.195	0.161	0.160	0.178	0.135	58
15.8	1.20	0.211	0.179	0.175	0.195	0.148	57
20.0	1.30	0.227	0.199	0.190	0.213	0.163	54
25.1	1.40	0.243	0.221	0.205	0.232	0.178	50
31.7	1.50	0.261	0.246	0.222	0.254	0.195	46
39.8	1.60	0.279	0.272	0.239	0.276	0.213	43
50.2	1.70	0.298	0.300	0.258	0.299	0.232	40
63.2	1.80	0.316	0.330	0.277	0.323	0.254	39
						Mean	50

by determining the fractional pressure increases at 5, 10, 15 and 20 minutes, and extrapolating back to zero time to get the initial rate of reaction. An inspection of Fig. 2 of Kassel's paper, however, shows that there is no uniform trend to the results with increasing increments of time, and within the experimental error virtually the same result is obtained by comparing values of $\Delta P_{20}/P_0$, as by comparing the initial rates.

In the present investigation it was found that efficiencies calculated from a comparison of fractional pressure increases at 5, 10 and 15 minutes showed no significant difference from those tabulated above. No appreciable error is therefore introduced by the use of fractional pressure increases at 20 minutes as a criterion of the relative rates of reaction.

Discussion

As mentioned at the outset, the previous investigation of the writer led to the conclusion that the cross-activation efficiency in mixtures of ethyl and methyl ether was zero, while that of Kassel indicated an efficiency of the order of 66 to 150 percent depending on the pressure. The present investigation gives values between these, *viz.*, 40 to 60 percent. It is almost certain that the discrepancies between the former investigations were due to temperature variations partially masking the effect under investigation. The values obtained in the present investigation should be considerably more reliable, on account of greatly improved thermostating.

In Fig. 3 the dotted curves indicate the values of $\Delta P_{20}/P_0$ for the mixture of ethers calculated on the basis of zero and 100 percent efficiency of energy transfer between unlike molecules. A comparison of these two curves with the experimental points indicates that a fair amount of reliance may be placed on the numerical values of the cross-activation efficiencies given above.

It may therefore be concluded: (a) that the contention of Kassel is borne out that collisions between unlike complex molecules are definitely effective in producing activation in unimolecular reactions; (b) that there is, however, a definite specificity of energy transfer, collisions between unlike complex molecules being considerably less effective than those between molecules of the same kind.

The Normal State of the Hydrogen Molecule-Ion*

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(Received March 16, 1933)

A variation function somewhat similar to that applied by Rosen to H_2 is used in the discussion of the normal state of H_2^+.

IN treating the normal state of the hydrogen molecule by the variational method, N. Rosen[1] used an eigenfunction involving the one-electron function

$$\psi=\psi^0+\sigma\psi',$$

in which $\psi^0=(\alpha^3/\pi)^{\frac{1}{2}}e^{-\alpha r_a}$ is a hydrogen-like $1s$ wave function for nucleus a, with effective nuclear charge (in units e) $Z=\alpha a_0$, and $\psi'=(\alpha^5/\pi)^{\frac{1}{2}}r_a e^{-\alpha r_a}\cos\theta_a$ is a hydrogen-like $2p$ function for nuclear charge $2Z$, θ_a being the angle between the nuclear axis and the radius vector from nucleus a to the electron, and σ a parameter. In order to see to what extent this method of treatment of molecules could be expected to be satisfactory in other cases, and whether or not pronounced improvement could be obtained by varying the ratio of the effective nuclear charges in ψ^0 and ψ', we have treated the hydrogen molecule-ion (which has previously been well investigated) by methods similar to Rosen's.

For this purpose we replace Z by $Z'=\epsilon Z$ in ψ'. ψ^0 and ψ' satisfy the equations

$$H_a^0\psi^0=Z^2E_0\psi^0 \quad \text{and} \quad H_a'\psi'=\epsilon^2Z^2E_0\psi',$$

where

$$H_a^0=\frac{-h^2}{8\pi^2m}\nabla^2-\frac{Ze^2}{r_a} \quad \text{and} \quad H_a'=\frac{-h^2}{8\pi^2m}\nabla^2-\frac{2Z\epsilon e^2}{r_a},$$

and are normalized and mutually orthogonal.

We write

$$\chi=\psi^0+\phi^0+\sigma(\psi'+\phi')$$

as the complete eigenfunction for the molecule-ion, with ϕ^0 and ϕ' replacing ψ^0 and ψ' for the nucleus b. The Hamiltonian for this problem is

$$H=\frac{-h^2}{8\pi^2m}\nabla^2+e^2\left(\frac{1}{R}-\frac{1}{r_a}-\frac{1}{r_b}\right).$$

The integrals arising from the expression for the energy

$$W=\int\chi H\chi d\tau\Big/\int\chi^2 d\tau$$

are listed below using Rosen's notation.

$$I_{00}=\int\psi^0\phi^0 d\tau, \quad F_1=\int\frac{(\psi')^2}{r_a}d\tau, \quad J_{00}=\int\frac{\psi^0\phi^0}{r_a}d\tau,$$

$$I_{01}=\int\psi^0\phi' d\tau, \quad G_{00}=\int\frac{(\psi^0)^2}{r_b}d\tau, \quad J_{01}=\int\frac{\psi^0\phi'}{r_a}d\tau,$$

$$I_{11}=\int\psi'\phi' d\tau, \quad G_{01}=\int\frac{\psi^0\psi'}{r_b}d\tau, \quad J_{10}=\int\frac{\psi'\psi^0}{r_a}d\tau,$$

$$F_0=\int\frac{(\psi^0)^2}{r_a}d\tau, \quad G_{11}=\int\frac{(\psi')^2}{r_b}d\tau, \quad J_{11}=\int\frac{\psi'\phi'}{r_a}d\tau.$$

The integrals (I_{01}, G_{01}, J_{01}, and J_{10}) not given in Rosen's paper were evaluated in elliptic coordinates and have the following forms in terms of ϵ and $\rho=\alpha R$:

$$I_{01}=(8\epsilon^{5/2}/(1-\epsilon^2)^4\rho^2)[e^{-\rho}\{(\epsilon^2-1)4\epsilon\rho^2-24\epsilon\rho-24\epsilon\}+e^{-\epsilon\rho}\{(1-\epsilon^2)^2\rho^3-8\epsilon\rho^2(1-\epsilon^2)+24\epsilon^2\rho+24\epsilon\}],$$

$$RJ_{01}=(4\epsilon^{5/2}/(1-\epsilon^2)^3\rho)[-8\epsilon e^{-\rho}(\rho+1)+e^{-\epsilon\rho}\{(1-\epsilon^2)^2\rho^3-4\epsilon(1-\epsilon^2)\rho^2+8\epsilon^2\rho+8\epsilon\}],$$

$$RJ_{10}=(8\epsilon^{5/2}/(1-\epsilon^2)^3\rho)[e^{-\rho}\{(1-\epsilon^2)\rho^2+4\rho+4\}+e^{-\epsilon\rho}\{(1-\epsilon^2)\rho^2-4\epsilon\rho-4\}],$$

$$RG_{01}=(4\epsilon^{5/2}/(1+\epsilon)^5\rho)[-e^{-(1+\epsilon)\rho}\{(1+\epsilon)^3\rho^3+4(1+\epsilon)^2\rho^2+8(1+\epsilon)\rho+8\}+8].$$

* Contribution from Gates Chemical Laboratory, California Institute of Technology, No. 363.

[1] N. Rosen, Phys. Rev. **38**, 2099 (1931).

The energy can be expressed as

$$W=2Z^2E_0A/d+2ZE_0B/d,$$

where

$$A=1+I_{00}+\sigma(1+\epsilon^2)I_{01}+\sigma^2\epsilon^2(1+I_{11})-(2/\rho)[RF_0+RJ_{00}+\sigma(RJ_{01}+2\epsilon RJ_{10})+2\epsilon\sigma^2(RF_1+RJ_{11})],$$

$$B=(2/\rho)[RF_0+RG_{00}-I_{00}-1+2RJ_{00}+2\sigma(RJ_{01}-I_{01}+RG_{01}+RJ_{10})+\sigma^2(RF_1-I_{11}+RG_{11}+2RJ_{11}-1)],$$

$$d=2[1+I_{00}+2\sigma I_{01}+\sigma^2(1+I_{11})].$$

This expression for the energy can be minimized with respect to Z, giving

$$Z=-B/2A,$$

which when combined with the expression for W gives

$$W=-E_0B^2/2dA.$$

Results

On placing $\epsilon=1$ and minimizing the energy relative to Z, σ, and ρ, the values $\epsilon=1$, $\rho=2.50$, $\sigma=0.1605$, $Z=1.2537$, and $W=-16.242$ volt-electrons were obtained. The value given for W by Burrau's[2] and Hylleraas'[3] exact treatments is -16.30 volt-electrons. Consequently the Rosen-type function leads to an error of 0.06 volt-electron, which is rather unsatisfactory, in view of the fact that Guillemin and Zener[4] obtained the value $W=-16.30$ volt-electrons by using a two parameter function no more complicated than the Rosen-type function.

It was thought that the error of 0.06 volt-electron in W might be removed by varying ϵ. On carrying out this variation for the values of σ, Z, and ρ given above, then varying σ, and finally varying ϵ again, there were obtained the values

$$\rho=2.50, \quad \epsilon=1.15, \quad \sigma=0.145,$$

$$Z=1.247, \quad Z'=1.434, \quad r_0=1.06\text{A},$$

and $W=-16.257$ volt-electrons. The discrepancy in the energy has, it is seen, been reduced by only one-third by the variation of ϵ, being still 0.04 volt-electron. (The value of r_0 obtained is the same as that found by Burrau and Hylleraas and also found experimentally for excited states of H_2.) We accordingly conclude that the Rosen-type function for the hydrogen molecule-ion is not so satisfactory as the Guillemin-Zener-type function of equivalent complexity, and that no pronounced improvement results from a variation of ϵ from 1. Change of Rosen's treatment for the hydrogen molecule by introducing ϵ in his function and varying it can hence be expected to lead to little improvement over his results.

It must be mentioned that the error in W of 0.04 volt-electron is only about 8 percent as great as that for a function with $\sigma=0$, i.e., involving $1s$ functions alone, for which Finkelstein and Horowitz[5] obtained $Z=1.228$, $r_0\leqq 1.06$A, and $W=-15.75$ volt-electrons, so that very marked improvement in the wave function is obtained by introducing the Rosen-type term ψ'.

[2] An account of this work is given by Linus Pauling, Chem. Rev. **5**, 173 (1928).

[3] E. A. Hylleraas, Zeits. f. Physik, **71**, 739 (1931).

[4] V. Guillemin and C. Zener, Proc. Nat. Acad. **15**, 314 (1929).

[5] B. N. Finkelstein and G. E. Horowitz, Zeits. f. Physik **48**, 118 (1928).

Lifetimes of Unstable Molecules

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The mechanism of the decomposition of a molecule formed by the collision between a molecule and another particle is discussed qualitatively. Calculations are then carried through to determine the lifetime of a simple linear triatomic molecule formed by the collision of an atom with a diatomic molecule. The results are applied to the short-lived molecule HO_2 to determine the order of magnitude of its lifetime in a number of different states, although it does not conform strictly to the idealized conditions for which the calculation was made.

I.

THERE is evidence that, as intermediate steps in certain chemical reactions, molecules are formed of extremely short lifetime, decomposing spontaneously unless they can react with other molecules before this happens. In some cases the molecules are known to be intrinsically stable. The question naturally arises as to the mechanism of this unimolecular decomposition. While this type of phenomenon has been treated by other writers,[1] it is the purpose of the present paper to discuss it in slightly greater detail than has been done hitherto and from a somewhat different point of view.

Let us first consider the formation of a molecule from two colliding particles. In order that they may form a stable system after the collision two conditions must be satisfied. First the force between the particles must be such that their potential energy as a function of the distance between them must have a minimum, that is, its graph must have the form of a valley. Then, the sum of this potential energy and the energy of relative motion of the particles must be less than the top of either side of the potential valley. It is evident that since the particles were originally free and therefore had energy above the outer wall of the potential valley there must be something to take up some energy in order to bind the particles to each other. As is well known, this can be done by a third particle (triple collision), the wall of the containing vessel, etc.

It must be remembered, however, that it is not necessary to remove this energy completely from the system. It is sufficient merely to transfer it from the degrees of freedom corresponding to the relative motion of the two particles to some other part of the system. Thus, if the colliding particles are both atoms the energy might go to excite the electrons in one or both of them, producing a molecule in an excited electronic state. If one of the particles is a molecule there is an additional way of disposing of this energy. It might be taken up by the internal degrees of freedom of this molecule as vibrational energy. It is this case that interests us in the present paper, namely, that in which a collision takes place between a molecule and an atom or another molecule so that some vibrations are excited in the former and a binding to the latter thus produced.

With this picture it is easy to see why the molecule, if left to itself, eventually may decompose. Just as the energy was able to flow from the coordinates of relative motion to some other portion of the system, so it may sometimes also flow back. If it does this, the energy of relative motion assumes its original value, the particles are once again free, and they promptly separate.

This sort of explanation appears quite reasonable, but how does one account for the ability of the energy to flow in this way? The answer is to be found in the type of force existing in a molecule. It is known that the forces between atoms

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[1] For example, Roginsky and Rosenkewitsch, Zeits. f. physik. Chemie **B10**, 47 (1930), Langer, Phys. Rev. **34**, 92 (1929), Kassel, J. Phys. Chem. **32**, 1065 (1928), etc., Rice, Phys. Rev. **34**, 1451 (1929), etc. The paper of Roginsky and Rosenkewitsch treats the problem for the standpoint of the Auger effect as is done in the present paper.

do not add vectorially and are not central.[2] The potential energy of a group of atoms is a complicated function of all the coordinates and, strictly speaking, cannot be written as a sum of functions of individual distances between pairs of atoms. Even if one assumes as an approximation that the last is possible—so that one can use for the individual functions those of the type occurring in diatomic molecules, as approximated by Morse[3] for example—one is still faced with the n-body problem. These facts imply that the wave equation for a group of atoms is not separable for any choice of coordinates. Now if the equation were separable in some set of coordinates the energy of the system would be the sum of a number of energies each due to motion involving one coordinate. Each of these energies would be constant in time and hence there would be no possibility of energy flowing from one coordinate to another. Since the equation is not separable, however, this is not the case. In solving the equation one must use approximate methods. One can choose a set of coordinates which render the equation nearly separable—that is, make it separable if one neglects some of the smaller quantities in the equation. If one solves this approximate equation and then introduces the previously neglected terms as perturbations one finds in certain cases just the flow of energy described before. This may occur, for example, if there are degeneracies in the unperturbed problem.

It is rather a coincidence for a degeneracy to occur in the discrete states of a vibrating system, that is, for two energy levels belonging to two different modes of vibration to coincide, although this is known to occur.[4] That discrete levels should coincide with continuous is quite common. In fact if the system contains two or more internal degrees of freedom the energy spectrum of each consisting of a group of discrete levels surmounted by a region of continuous energy, there *must* be certain discrete energy levels which coincide with continuous energies. This can be seen in Fig. 1, where hypothetical potential curves have been drawn for two coordinates so that the zero of each is taken as the value of the potential energy at an infinite distance from the origin. The total energy is the sum of the energies for the two coordinates. If now we take a

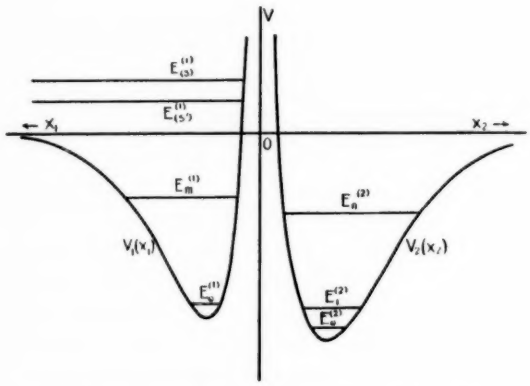

FIG. 1. Some energy levels in a system of two degrees of freedom, illustrating degeneracies between discrete and continuous states.

pair of energy levels $E_m^{(1)}$ and $E_n^{(2)}$ such that their sum is greater than $E_0^{(2)}$, one can always find a continuous level $E_{(s)}^{(1)}$ such that

$$E_{(s)}^{(1)}+E_0^{(2)}=E_m^{(1)}+E_n^{(2)}.$$

If $E_m^{(1)}+E_n^{(2)}$ is sufficiently high there may be a number of such levels. Thus in Fig. 1, $E_{(s')}^{(1)}$ and $E_1^{(2)}$ represent another such pair.

In the problem we are considering, since the molecule was formed through a collision of two free particles, the "bound" or discrete state into which it goes (neglecting the possibility of energy being radiated, which is slight) must coincide in energy with at least one continuous state, namely, that in which the particles were before the molecule was formed.

That being the case, there is a certain probability for a transition from the discrete state to a continuous one of the same energy—which is a dissociation of the system. This effect in a polyatomic molecule is analogous to the Auger effect for an atom or "predissociation" for a diatomic molecule, and the method of calculating transition probabilities is therefore already available.[5] The molecule may be said to have a

[2] London, *Probleme der modernen Physik*, p. 103, Leipzig (1928), Slater, Phys. Rev. **38**, 1109 (1931), Dennison, Rev. Mod. Phys. **3**, 280 (1931).

[3] Morse, Phys. Rev. **34**, 57 (1929).

[4] For example in CO_2, cf. Fermi, Zeits. f. Physik **71**, 250 (1931).

[5] Wentzel, Phys. Zeits. **29**, 321 (1928).

certain lifetime, i.e., the mean time required for it to dissociate. If this lifetime is sufficiently long so that the molecule can collide with other particles before dissociating it may give up its excess energy and become a completely stable system.

A case closely related to the one being considered at present is the following. There are many polyatomic molecules the atoms of which are arranged in groups such that the atoms in each group are bound together rather tightly but the groups are held together quite loosely. By a tight binding is ordinarily meant that a plot of the potential has a large curvature near its minimum. This in general implies that the potential valley is deep; whereas a loose binding has a shallow minimum and relatively little energy is required to cause dissociation. Now if such a molecule takes part in a collision as a result of which it receives sufficient energy to break one of the weak bonds, it may happen that this energy is first taken up by one of the strong bonds and is present as vibrational energy. After some time has elapsed this energy may reach the weak bond (in the manner discussed before) and cause a decomposition of the molecule. Such an effect is of rather frequent occurrence because the weak bonds are often in the interior of the molecule and thus less exposed to direct effects of collisions than some of the strong bonds. This process represents a very general type of unimolecular reaction. It is not easy to do much of a detailed quantitative nature for this case as yet, but perhaps the simple example treated in the following section may throw some light on the more general problem.

II.

1. General treatment

We now proceed to treat quantitatively a very simple idealized case, our purpose being to determine the order of magnitude of the lifetime of a molecule having an excess of energy. It is hoped that in spite of the simplification the essential features of the problem are retained.

Let us suppose a triatomic molecule with atoms of masses m_1, m_2 and m_3, restricted to move along a single straight line and let their distances from some fixed point on the line be x_1, x_2 and x_3 ($x_1<x_2<x_3$). We make the simplifying assumption that the potential energy

$$U=V_1(x_2-x_1)+V_2(x_3-x_2)+V_3(x_3-x_1), \quad (1)$$

where, for an equilibrium configuration, $|V_1|$ and $|V_2|$ are large compared to V_3. It is to be expected that V_1 and V_2 will have forms similar to those of stable diatomic-molecule potentials, whereas in general V_3 will correspond to a repulsive force.

If we write the wave equation for the system, introduce new variables

$$\left.\begin{aligned} r_1&=x_2-x_1,\\ r_2&=x_3-x_2,\\ \rho&=(m_1x_1+m_2x_2+m_3x_3)/(m_1+m_2+m_3),\end{aligned}\right\} \quad (2)$$

and take the wave function as a product $\psi(r_1, r_2)\chi(\rho)$, the terms depending on ρ can be separated off (giving the usual equation for the center of gravity of the system) and the equation for ψ becomes

$$\left\{-\frac{h^2}{8\pi^2}\left[\frac{1}{\mu_1}\frac{\partial^2}{\partial r_1^2}+\frac{1}{\mu_2}\frac{\partial^2}{\partial r_2^2}-\frac{2}{m_2}\frac{\partial^2}{\partial r_1\partial r_2}\right]+V_1(r_1)+V_2(r_2)+V_3(r_1+r_2)\right\}\psi=E\psi, \quad (3)$$

where E is the internal energy of the system and

$$\mu_1=m_1m_2/(m_1+m_2), \quad \mu_2=m_2m_3/(m_2+m_3). \quad (4)$$

To solve this equation exactly is impossible.[6] One notices however that if one omits the terms $(h^2/4\pi^2m_2)\partial^2\psi/\partial r_1\partial r_2$ and V_3 the problem reduces to solving the two ordinary equations

$$-(h^2/8\pi^2\mu_1)d^2\phi_m^{(1)}/dr_1^2+V_1\phi_m^{(1)}=E_m^{(1)}\phi_m^{(1)}, \quad (5)$$

$$-(h^2/8\pi^2\mu_2)d^2\phi_n^{(2)}/dr_2^2+V_2\phi_n^{(2)}=E_n^{(2)}\phi_n^{(2)}, \quad (6)$$

the solution of (3) being then

$$\left.\begin{aligned}\psi_{mn}^{0}&=\phi_m^{(1)}\phi_n^{(2)},\\ E_{mn}^{0}&=E_m^{(1)}+E_n^{(2)}.\end{aligned}\right\} \quad (7)$$

[6] For small vibrations one could introduce normal coordinates to get a good approximation. This cannot be done in the present case where dissociation is considered.

These quantities will be the more nearly equal to the correct ones the larger m_2 and the smaller V_3. The operator

$$T=(h^2/4\pi^2m_2)\partial^2/\partial r_1\partial r_2+V_3, \tag{8}$$

which has been omitted can now be introduced as a perturbation.

The quantity V_3, as has already been said, is in general small. Its effect as a perturbation will be to change the energy levels somewhat and it will also act to some extent as a coupling between the two vibrations characterized by Eqs. (5) and (6). However there are few cases in which one knows the value of V_3. Since furthermore its presence is hardly likely to affect the order of magnitude of the result we shall not give it much attention, but shall center our interest on the first term of T. The effect of this on the energy is zero by a first-order calculation if the wave functions are real, as is the case here. Its principal rôle is as a coupling between the vibrations, the physical interpretation being that, as the central atom moves in both vibrations, it transfers energy from one to the other.

To calculate the rate of transition from a discrete state to one in the continuous spectrum of the same energy we use the relation[5]

$$\Gamma=(4\pi^2/h)\,|\int\int\psi_{mn}{}^0T\psi_{(s)k}{}^0dr_1dr_2\,|^2, \tag{9}$$

where $\psi_{mn}{}^0$ is the wave function for the discrete state and $\psi_{(s)k}{}^0$ for the continuous state

$$\psi_{(s)k}{}^0=\phi_{(s)}{}^{(1)}\phi_k{}^{(2)}, \tag{7a}$$

$\phi_{(s)}{}^{(1)}$ denoting a wave function which is a solution of Eq. (5) for continuous energy $E_{(s)}{}^{(1)}$, (i.e., $E_{(s)}{}^{(1)}>0$). The transition rate Γ is related to the mean lifetime of the molecule τ by

$$\tau=1/\Gamma. \tag{10}$$

2. Numerical calculation

In order to evaluate (9) we must first get solutions of (5) and (6). For V_1 and V_2 we take the form suggested by Morse[3] for diatomic molecules

$$\left.\begin{aligned}V_1&=D_1e^{-2a_1(r_1-r_{01})}-2D_1e^{-a_1(r_1-r_{01})},\\ V_2&=D_2e^{-2a_2(r_2-r_{02})}-2D_2e^{-a_2(r_2-r_{02})},\end{aligned}\right\} \tag{11}$$

Further we might choose

$$V_3=D_3e^{a_3(r_1+r_2)} \tag{12}$$

in accordance with our general ideas about interatomic forces.

In solving (5) and (6) we need our function in a somewhat different form from that given by Morse and therefore briefly re-derive the solution of the equation

$$d^2\psi/dr^2+(8\pi^2\mu/h^2)(E-De^{-2a(r-r_0)}+2De^{-a(r-r_0)})\psi=0. \tag{13}$$

We make the following substitutions:

$$z=(4\pi/ah)(2\mu D)^{\frac{1}{2}}e^{-a(r-r_0)}, \tag{14}$$

where we assume that the range of z is 0 to ∞ (instead of 0 to $(4\pi/ah)(2\mu D)^{\frac{1}{2}}e^{ar_0}$), the error being small as Morse pointed out,

$$\left.\begin{aligned}\psi&=z^{-\frac{1}{2}}y,\\ k&=(2\pi/ah)(2\mu D)^{\frac{1}{2}},\\ m&=(2\pi/ah)(-2\mu E)^{\frac{1}{2}},\end{aligned}\right\} \tag{15}$$

and (13) becomes

$$d^2y/dz^2+\{-1/4+k/z+(1/4-m^2)/z^2\}y=0, \tag{16}$$

which is the confluent hypergeometric equation.[7]

For large values of z one solution is $W_{k,\,m}(z)$ which has the asymptotic form

$$W_{k,\,m}(z)\sim e^{-z/2}z^k\{1+[m^2-(k-\tfrac{1}{2})^2]/z+\cdots\}, \tag{17}$$

and the other independent solution is $W_{-k,\,m}(-z)$ which obviously does not have the proper behavior. We therefore take for our wave function $z^{-\frac{1}{2}}W_{k,\,m}(z)$.

We next consider small values of z. The two solutions there are $M_{k,\,m}(z)$ given by

$$M_{k,\,m}(z)=e^{-z/2}z^{m+\frac{1}{2}}\{1+[(\tfrac{1}{2}+m-k)/(2m+1)!]z+\cdots\}, \tag{18}$$

and $M_{k,\,-m}(z)$. If $E<0$, so that m is real and positive, the appropriate solution is $M_{k,\,m}(z)$, since the other function causes a singularity in ψ at the origin. Now we have the relation[7]

$$W_{k,\,m}(z)=[\Gamma(-2m)/\Gamma(\tfrac{1}{2}-m-k)]M_{k,\,m}(z)+[\Gamma(2m)/\Gamma(\tfrac{1}{2}+m-k)]M_{k,\,-m}(z), \tag{19}$$

[7] Whittaker and Watson, Modern Analysis, p. 337, Cambridge, 1927.

and so our quantization condition is

$$\Gamma(2m)/\Gamma(\tfrac{1}{2}+m-k)=0,$$

or

$$\tfrac{1}{2}+m-k=-n \quad (n=0,\ 1,\ 2,\ \cdots) \tag{20}$$

subject to the restriction $m>0$.

We have then for the discrete states

$$\begin{aligned}\psi_n &= z^{-\frac{1}{2}}W_{k,\,k-n-\frac{1}{2}}(z)=(-1)^n[\Gamma(2k-n)/\Gamma(2k-2n)]z^{-\frac{1}{2}}M_{k,\,m}(z),\\ &=(-1)^n\Gamma(2k-n)e^{-z/2}z^{k-\frac{1}{2}-n}\sum_{j=0}^{n}(-1)^j\binom{n}{j}z^j/\Gamma(2k-2n+j),\end{aligned} \tag{21}$$

which is essentially the same as the solution used by Morse.

For $E>0$, m is imaginary and there is no restriction on it. We need the asymptotic form of ψ as $r\to\infty$ or $z\to 0$. Expanding (19) and keeping terms of greatest order of magnitude, one finds

$$\psi_{(s)}\sim 2G\cos(sar-s\lambda+\gamma), \tag{22}$$

where

$$\left.\begin{aligned}&s=m/i=(2\pi/ah)(2\mu E)^{\frac{1}{2}},\\ &\Gamma(2is)/\Gamma(\tfrac{1}{2}-k+is)=Ge^{i\gamma}\\ \text{and}\quad&\lambda=ar_0+\ln(4\pi(2\mu D)^{\frac{1}{2}}/ah).\end{aligned}\right\} \tag{23}$$

If one now normalizes the wave function with respect to the energy (Appendix, 1, 2) the normalizing factor by which it must be multiplied is found to be

$$N_{(s)}=(4/h)(\mu\sinh 2\pi s\,|\,\Gamma(\tfrac{1}{2}-k+is)\,|^2/a)^{\frac{1}{2}}. \tag{24}$$

To normalize the discrete wave function, we first evaluate a general integral we shall need. We find (Appendix, 3)

$$\int\psi^{(m)}\psi_n z^\lambda dz/z=n!\Gamma(2k-n)\sum_{j=0}^{n}\frac{(-1)^j\Gamma(k-\frac{1}{2}-m+\lambda-j)\Gamma(k-\frac{1}{2}+m+\lambda-j)}{j!(n-j)!\Gamma(2k-n-j)\Gamma(\lambda-j)}, \tag{25}$$

where ψ_n is a discrete wave-function and $\psi^{(m)}$ an arbitrary one.[8] For $m=k-\frac{1}{2}-n$ and $\lambda=0$ one finds that the normalizing factor for the discrete function is

$$N_n=[(2k-2n-1)a/(n!\Gamma(2k-n))]^{\frac{1}{2}}. \tag{26}$$

If now one makes use of the easily derivable relation

$$\begin{aligned}&\int\psi_k(d\psi_n/dr)dr\\ &=\int\psi_k\psi_n(dV/dr)dr/(E_n-E_k),\ (E_n\neq E_k)\end{aligned} \tag{27}$$

and observes that

$$dV/dr=(a^2h/2\pi)[(D/2\mu)^{\frac{1}{2}}z-(ah/8\pi\mu)z^2], \tag{28}$$

one finds with the help of (25) that the transition rate from a discrete state with approximate wave function $\psi_{pm}{}^0$ to a continuous state with function $\psi_{(s)n}{}^0$ (if we neglect V_3 in (8))[9] is

$$\Gamma=(h\mu_1a_2^2/4m_2^2)F_1(s)F_2(m)G_1(p)G_2(n),\qquad (n<m) \tag{29}$$

where

$$\left.\begin{aligned}F_1(s)&=|\Gamma(k_1+\tfrac{1}{2}+is)|^2\sinh 2\pi s\\ &\quad\div(\sinh^2\pi s+\cos^2\pi k_1),\\ &\sim 2|\Gamma(k_1+\tfrac{1}{2}+is)|^2\quad\text{for}\quad s\gtrsim 1,\\ F_2(m)&=m!\Gamma(2k_2-m)(2k_2-2m-1),\\ G_1(p)&=(2k_1-2p-1)/(p!\Gamma(2k_1-p)),\\ G_2(n)&=(2k_2-2n-1)/(n!\Gamma(2k_2-n)).\end{aligned}\right\} \tag{30}$$

[8] The notation here is exceptional because the wave function is intended to correspond to either a discrete or a continuous state and the superscript is the m defined in (15). Everywhere else as far as the appendix, a subscript in parentheses indicates a continuous state and is the value of s as defined in (23); without parentheses it indicates a discrete state and is the value of the integer in (20).

[9] If one wished to take into account the effect of V_3 on the rate of transition, it could be done by writing (12) in terms of z_1 and z_2 (in analogy with (14)) and then making use of the integral (25). This is not done here for the reasons previously stated.

The quantities s, n, p and m are connected by the fact that the energy of the two states must be the same, which leads to the relation

$$(a_1^2/\mu_1)(s^2+(k_1-p-\tfrac{1}{2})^2) = (a_2^2/\mu_2)((k_2-n-\tfrac{1}{2})^2-(k_2-m-\tfrac{1}{2})^2). \quad (31)$$

To evaluate (30) we need to know that[10]

$$|\Gamma(k_1+\tfrac{1}{2}+is)|^2 = [\Gamma(k_1+\tfrac{1}{2})]^2/\prod_{j=0}^{\infty}(1+s^2/(k_1+\tfrac{1}{2}+j)^2). \quad (32)$$

It can be seen from (30) and (32) that if there are several continuous states to which the system can go, the transition probability is by far the greatest to that state which involves the least change in the energy of either individual vibration (except that if s is very small there is a strong dependence on $\cos \pi k_1$, and predictions are difficult, but this is rather unusual).

Let us now suppose that the molecule was formed by the collision of atom 1 with the diatomic molecule A consisting of atoms 2 and 3, each having kinetic energy of the order of magnitude of that for room temperature; and let us suppose further that as result of the collision the vibration of 2 and 3 changed from $n=0$ to some quantum number m, and a vibration of 1 and 2 with quantum number p was set up. We must assume that the original relative kinetic energy is such that it matches with the molecular levels, i.e., (31) is satisfied. We are not concerned with the details of the molecule formation, and if we like can assume that a large number of elastic collisions take place until the energy match occurs.[11]

Then in the decomposition of the molecule the process is uniquely defined. We have $n=0$, s is proportional to the initial relative momentum of the particles 1 and 2, as in (23), and p is an integer satisfying (31). For this case the transition rate becomes

$$\Gamma = (h\mu_1 a_2^2/4m_2^2)F_1(s)G_1(p)F_2(m)/\Gamma(2k_2-1). \quad (29a)$$

If further we neglect the denominator of (32) this can be written

$$\Gamma = \frac{h\mu_1 a_2^2}{2m_2^2}\,\frac{(2k_1-2p-1)[\Gamma(k_1+\tfrac{1}{2})]^2 m!(2k_2-2m-1)\Gamma(2k_2-m)}{p!\Gamma(2k_1-p)\Gamma(2k_2-1)}. \quad (29b)$$

If we set $k_1-p-\tfrac{1}{2}=t$ we get

$$\Gamma = \frac{h\mu_1 a_2^2 t(2k_2-2m-1)[\Gamma(k_1+\tfrac{1}{2})]^2 m!\Gamma(2k_2-m)}{m_2^2\Gamma(k_1+\tfrac{1}{2}-t)\Gamma(k_1+\tfrac{1}{2}+t)\Gamma(2k_2-1)}. \quad (29c)$$

In this form we see that Γ is not as sensitive in the dependence of its order of magnitude on k_1 and k_2 as appeared in the earlier formula. An estimate of Γ may have some reliability (as far as order of magnitude) even if there are moderate uncertainties in these constants.

A compound HO_2 is believed to be formed bimolecularly by the reaction of atomic hydrogen with molecular oxygen. It is probably not a linear molecule and one does not know what the constants of its potential functions are. We shall assume that the above model can be used nevertheless; and for potential functions we use those supposed to exist in the lowest electronic states of OH and O_2 on the basis of their vibrational spectra. It is hoped that the order of magnitude of the result will not be changed very much by these approximations.

We take therefore μ_1, μ_2, $m_2=(16/17,\ 8,\ 16)\times 1.65\cdot 10^{-24}$ g, $k_1=25.5$, $k_2=68.5$, $a_1=2.0\cdot 10^8$ cm^{-1}, $a_2=2.34\cdot 10^8$ cm^{-1}. At ordinary temperatures s is of the order of magnitude of 1. A simple calculation leads to the results in Table I.

We see that for $m=1$, the calculated lifetime is so short that one really cannot speak of the molecule having existed, for the entire process could not be distinguished from an elastic collision. For m greater than 4, the lifetime is very long compared to the average time between

[10] Nielsen, *Handbuch der Gammafunktion*, p. 23, Leipzig (1906).

[11] This matching of energy is not very difficult because of the broadening of the levels due to the finite lifetimes of the molecular states. Roughly the ratio of favorable to total number of collisions is of the order of magnitude of $h\Gamma/\Delta E$ where ΔE is the spacing of the vibrational levels in the energy region involved.

collisions at moderate pressures. The mean lifetime would depend on the collision process which would determine the relative frequency of occurrence of the various values of m. Because collisions (and consequent reactions) would play a part in determining the actual lifetime for the larger values of m, an experimentally obtained value for the mean lifetime would involve a certain amount of arbitrariness in its interpretation. The results calculated here are at any rate consistent with available chemical data.[12]

TABLE I.

m	p	l	s	$\Gamma(\text{sec.}^{-1})$
1	21	4	2.4	$2\cdot10^{14}$
2	19	6	2.7	$2\cdot10^{12}$
3	17	8	0.5	$2\cdot10^{10}$
4	16	9	2.0	$4\cdot10^{8}$

3. Conclusion

Aside from the simplification of the conditions in the previous calculation, a further difficulty is that the unperturbed wave functions do not describe the actual situation very well (especially for the continuous states) and the perturbation may be quite large so that a first order method of treatment may be inaccurate. However, one would expect the order of magnitude to be unchanged in a more accurate treatment. Also it must be stressed that the purpose of the calculation is mainly to see how the process can come about. The particular type of coupling between the two unperturbed vibrations does not matter very much. The essential point is that in any treatment of the problem some sort of coupling will be found to exist—and it is to be expected that it will in general play a part in bringing about the decomposition of the molecule.

In conclusion the writer wishes to express his indebtedness to Professor J. R. Bates, who called attention to this type of problem, for discussions on the chemical aspects of the subject, and to Professor D. M. Dennison for discussions on the physical aspects.

APPENDIX

1. Normalization of continuous wave functions

The well-known condition for normalization of a continuous wave function in a one-dimensional problem where the variable has a range 0 to ∞ is:

$$J=\lim_{\Delta\to 0}(1/\Delta)\int_0^\infty\left[\int_{p-\Delta/2}^{p+\Delta/2}\psi_p(x)dp\right]\left[\int_{p-\Delta/2}^{p+\Delta/2}\psi_p(x)dp\right]dx=1, \tag{33}$$

where p is a continuous parameter used to order the wave functions.

Let us write

$$\psi_p=\phi_p+\chi_p, \tag{34}$$

where χ_p is that part of the wave function which goes to zero with sufficient rapidity as $x\to\infty$ so that $\int_0^\infty\bar{\chi}_p\chi_p dx$ and $\int_0^\infty\bar{\phi}_p\chi_p dx$ are both convergent. Let us now write J as the sum of two integrals, one for a finite range 0 to a and the second for the range a to ∞. Then in the first integral and in all the terms of the second which involve χ_p or $\bar{\chi}_p$ the order of integration can be interchanged and these quantities are seen to vanish. We have therefore

$$J=\lim_{\Delta\to 0}(1/\Delta)\int_a^\infty\left[\int_{p-\Delta/2}^{p+\Delta/2}\bar{\phi}_p(x)dp\right]\left[\int_{p-\Delta/2}^{p+\Delta/2}\phi_p(x)dp\right]dx, \tag{35}$$

where a is finite but can be made as large as one pleases. Practically this means that one can use the *asymptotic form* of the wave function in carrying out a normalization.

2. Normalization with respect to energy

The normalizing factor for a continuous wave function depends on the parameter used. Care must be taken to use the same parameter consistently. Thus in the original derivation of (9) the energy was the parameter and integrations were carried out with respect to it. It is therefore necessary to use the energy in normalizing the function in our case.

If we consider the wave function for a free particle $e^{2\pi ikx}$ where

$$k=P/h=(2\mu E)^{\frac{1}{2}}/h, \tag{36}$$

P is the momentum of the particle and the range of x is 0 to ∞, the usual normalization with respect to k leads to a normalizing factor, $2^{\frac{1}{2}}$. If, instead, we use E as parameter

[12] Bates and Lavin, J. Am. Chem. Soc. **55**, 81 (1933); Bates and Salley, ibid., p. 110.

the integration is somewhat more complicated and leads to a normalizing factor

$$N=(1/h)(2\mu/k)^{\frac{1}{2}}=(2\mu/Ph)^{\frac{1}{2}}. \tag{37}$$

For $\cos 2\pi kx$ this is to be multiplied by $2^{\frac{1}{2}}$. Use was made of it in (24).

3. Evaluation of an integral

To evaluate the integral (25) use is made of Eq. (19). In the course of the calculation one obtains two hypergeometric series for argument 1. These can be summed if $\lambda<1$. If $1<\lambda<2$, one can make use of the well-known relations between hypergeometric functions and by letting the argument approach 1, one obtains the same result as before. One thus finds that (25) is valid for $\lambda<1$ and $1<\lambda<2$. But since (25) is analytic for $0\leqslant\lambda\leqslant 2$ it must give the correct values at $\lambda=1$ and $\lambda=2$ also.

The Lattice Energies of the Silver and Thallium Halides*

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The lattice energies and lattice constants of the silver and thallium halides are calculated assuming ionic crystals with a van der Waals potential. The latter term, which is large, accounts for the low solubilities (high lattice energies) of the salts. The calculations appear to be quantitatively satisfactory for the thallium halides, TlCl, TlBr and TlI, and for the three silver halides AgF, AgCl and AgBr. Definite evidence is found for assuming the existence of a homopolar potential in AgI of about 10 percent of the total lattice energy. One reason for believing this, is the stability of the zincblend instead of the rocksalt lattice, which latter should be stable were the compound purely ionic. There is presumably some homopolar binding in AgBr but it cannot be large. The thallium salts probably are entirely ionic. The theoretically calculated and experimental (chemical) lattice energies are, respectively, in K cal., AgF, 219, 217.7; AgCl, 203, 205.7; AgBr, 197, 201.8; AgI, 190, 199.2; TlCl, 167, 170.1; TlBr, 164, 165.6; TlI, 159, 160.8.

INTRODUCTION

THE lattice energy of a uni-univalent ionic crystalline salt, namely the energy change at 0°K of the reaction $MX_{cryst.} \rightarrow M_{gas}^{+} + X_{gas}^{-}$, can be calculated as the sum of the heats of a number of reactions. A series of reactions which may be used is shown in Table II. The energy so obtained might be termed the experimental lattice energy. If, for the silver and thallium halides, these experimental lattice energies are compared with the electrostatic energies, it is found that the former are almost as large as, or even larger than the latter. The electrostatic potential is purely attractive, and in addition to it there must exist in a crystal another potential whose first and second derivatives with respect to the lattice constant r (for a uniform increase in all crystal dimensions) at the experimental equilibrium value of $r = r_0$ may be obtained from the value of r_0 and the compressibility respectively.

If this potential of known first and second derivatives is assumed to be purely repulsive and simple in form (that is the potential $V(r) \geq 0$ and $\partial V/\partial r \leq 0$ for all values of r, and $\partial V/\partial r$ and $\partial^2 V/\partial r^2$ both vary fairly slowly with r), it is impossible to account for the experimental lattice energy to within 15 or 20°K cal. for these salts. This means that the remaining non-electrostatic potential is partially attractive, it takes negative values at some r. It is frequently assumed that this behavior is to be accounted for by the existence of homopolar forces in these crystals.

There is an additional calculable attractive potential besides the electrostatic, the van der Waals potential. Its magnitude can be computed from equations developed by London[1] and by Margenau.[2] The calculation used here will follow closely a discussion by the author for the alkali halides.[3] If the van der Waals potential is included with the electrostatic, the remaining potential may be assumed to be purely repulsive and the calculated lattice energies agree well for all but AgI with the experimental values. The method of calculation of the lattice energy follows closely the method of Born and Mayer,[4] whose paper shall be referred to in the succeeding paragraphs as B.M. The results of this paper, then, show that the homopolar contribution to the lattice energies of AgF, AgCl, AgBr, TlCl, TlBr and TlI is practically insignificant, and that in AgI is small and can be estimated.

CALCULATION OF THE VAN DER WAALS POTENTIAL

The equations used in calculating the potential are the following:

* A preliminary report was presented at the *Congress on The Solid State at Leningrad*, September, 1932.

[1] F. London, Zeits. f. physik. Chemie **B11**, 222 (1930).

[2] H. Margenau, Phys. Rev. **38**, 747 (1931).

[3] J. E. Mayer, J. Chem. Phys. **1**, 270 (1933). See April number.

[4] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932).

$$U_v = U_{dd} + U_{qd} = -C/r^6 - D/r^8, \quad (1)$$

$$C = S_6' c_{+-} + S_6''(c_{++} + c_{--})/2,$$
$$D = S_8' d_{+-} + S_8''(d_{+-} + d_{--})/2, \quad (2)$$

$$c_{ij} = \frac{2}{3} e^4 \frac{Q_{i00}^2 Q_{j00}^2}{\epsilon_i + \epsilon_j}, \quad d_{ij} = \frac{3}{2} c_{ij} \left(\frac{Q_{i00}^2}{p_i} + \frac{Q_{j00}^2}{p_j} \right), \quad (3)$$

$$Q_{i00}^2 = \frac{3}{2} \frac{\alpha_i \epsilon_i}{e^2}. \quad (4)$$

The complete van der Waals potential in the crystal U_v, is additively composed of a dipole-dipole term U_{dd} varying as r^{-6} and a quadrupole-dipole term U_{qd} varying as r^{-8}, with constants respectively C and D. C and D can be calculated from the corresponding c_{ij}'s and d_{ij}'s, the constants for two ions i and j. In order to make the calculations the sums S_6', S_6'', S_8', S_8'' must be known, which are the sums of l^{-6} and l^{-8} over the odd (unlike) and even (like) points of the lattice, respectively, if l is the distance between the lattice points. The sums depend on the lattice type and on the arbitrary choice of r, which here and in the following, is understood to be the shortest geometrical constant of the lattice, the distance between unlike neighboring ions. The sums can be easily computed from a table of similar sums given by Lennard-Jones and Ingham.[5] The constants c_{ij} and d_{ij} for the potential between two ions i and j can be calculated from the polarizabilities α and the energies ϵ of the ions in the crystal in question. ϵ is an energy corresponding to a weighted average frequency of the absorption of the ion in the crystal.[3] For the positive ions the polarizability α and the energy ϵ are presumed to be practically constants of the ions independent of the crystal. ϵ is given the value 90 percent of the ionization potential of the gaseous ion (the second ionization potential of the element). For the negative ions α is supposed to be inversely proportional to ϵ, and ϵ is to be obtained from the experimental ultraviolet absorption of the crystal. This assumption sets Q_{00}^2, the 00 matrix element of the sum of the q^2 for all electrons, a sort of area of the ion, as being independent of the crystal. The value of Q_{00}^2 for the halide ions has been calculated from the alkali halides.[3] p, the number of outer electrons, is taken as the geometric mean of the theoretical (Periodic Table) value, and one calculated from the polarizability and frequency.

For the silver halides the values of ϵ for the negative ions have been chosen after an examination of the absorption curves for the chloride, bromide, and iodide. The value of the polarizability α in the crystal has been calculated by the use of Q_{00}^2 and ϵ with Eq. (4). Pauling's[6] value $\alpha = 1.72 \times 10^{-24}$ cm^3 has been used for Ag^+ and the sums of the negative and positive polarizabilities, row 7, Table I, has been compared with the experimental value, row 8, calculated from the index of refraction n for yellow light. These experimental values of $\sum\alpha$ (yellow) may be expected to be some 5 percent or more higher than those which would be calculated were the index of refraction extrapolated to $\lambda = \infty$. An estimated value of $\sum\alpha(\lambda = \infty)$ is given in row 9. The agreement indicates only that no great error has been made in the choice of constants.

For the thallium halides the value $\alpha = 3.50 \times 10^{-24}$ cm^3 for Tl^+ ion is chosen from an examination of the index of refraction of some complex thallium salts and the corresponding alkali salts. The values of ϵ for the negative ions are chosen to be in agreement with those of the silver salts.

The choice of values for all these constants is subject to considerable uncertainty. For the silver salts the van der Waals potential may be in error by as much as 30 percent of its value. For the thallium salts the error may be even larger. The author has attempted not to err in such a way as to make the potential too large. It is felt that the actual potential is more likely to be greater than to be smaller than the values calculated here. Owing to the use of an empirical repulsive potential, determined from the attractive potential and the constants of the crystal, the magnitude of the error introduced into the computation of the lattice energy by an error in the assumed values of C, and especially of D, is less than that introduced into the van der Waals potential. That is, if the value of $U_{dd} = -C/r^6$ were assumed to be 3 k cal. greater than the values here given, say for AgF, the total

[5] J. E. Jones and A. E. Ingham, Proc. Roy. Soc. (London) **A107**, 636 (1925).

[6] L. Pauling, Proc. Roy. Soc. (London) **A114**, 181 (1927).

calculated lattice energy would be only 1.5 k cal greater.

The Repulsive Potential and the Lattice Energy

The compressibilities, β, of AgCl, AgBr, AgI, TlCl and TlBr are given in *International Critical Tables*. The thermal expansion for AgCl and AgBr is also given there. The term $(3T/N\beta)(\partial v/T)$, in which the thermal expansion is needed, is small, and its value can be estimated for the other salts without introducing any appreciable error. From these data and the lattice constant, r_0, which is taken from the *Strukturbericht*[7] the repulsive potential is computed. The method deviates from that of B.M. only in so far that for the silver salts it is not assumed that the exponents for the repulsive potential between two Ag^+ ions and two halide ions, or an Ag^+ ion and a halide ion, are the same.

If the repulsive potential energy of the crystal as a function of r is written $B(r)$ it has been shown that, at $r=r_0$, the lattice constant at temperature T, and $P=0$,

$$-r_0\frac{dB(r_0)}{dr}=\frac{\alpha e^2}{r_0}+\frac{6C}{r_0^6}+\frac{8D}{r_0^8}-\frac{3T}{N\beta}\left(\frac{\partial V}{\partial T}\right)=\tau, \quad (5)$$

$$r_0^2\frac{dB(r_0)}{dr^2}=\frac{2\alpha e^2}{r_0}+\frac{42C}{r_0^6}+\frac{72D}{r_0^8}+\frac{9V}{N\beta}=\sigma. \quad (6)$$

These equations differ from those in B.M. only in the inclusion of the D-term and the omission of a factor multiplying $9V/N\beta$ in Eq. (6). This factor always has a value very close to 1.

It is now assumed that the replusive potential between two ions i and j, $b_{ij}(r_{ij})$ is given by the equation,

$$b_{ij}=c_{ij}bb_ib_je^{-r_{ij}/\rho_{ij}}, \quad (7)$$

with

$$\begin{aligned}\rho_{ij}&=\rho_i+\rho_j,\\ 2\rho_{H^-}&=\rho_-=0.345\times10^{-8}\text{ cm},\\ 2\rho_{Ag^+}&=\rho_+,\\ \rho_{H^-}+\rho_{Ag^+}&=\rho.\end{aligned} \quad (8)$$

Eq. (7) is that used in B.M. and Eq. (8) is introduced to allow for the fact that not all ion pairs show the same value ρ_{ij}, which, however, was the case for the alkali halides. There is some reason to believe that Eq. (8) is justified. It is sufficient here to point out that the same repulsion is assumed between two negative ions that was found in the alkali halides. The repulsion between the positive ion pairs is negligible for all silver salts on this, or any other reasonable assumption, and the value of ρ_+ is in reality never used. The value of ρ, the repulsive exponent between an Ag^+ and a halide ion, is calculated from the compressibility, and the assumptions used are relatively unimportant in influencing the value obtained. That is, actually Eq. (8) is entirely unimportant, the repulsion between Ag^+ pairs is probably negligible and is neglected, that between halide pairs is assumed to be the same function of r as in the alkali halides, and that between Ag^+ and halide ions is calculated from the constants of the crystal.

Defining as M the number of unlike neighbors of any lattice point, as M' the number of like "next-to-neighbors," as a the ratio of the distance between next-to-neighbors to that between neighbors, and with $c_1=c_{++}/c_{+-}$, $c_2=c_{--}/c_{+-}$, the relative effect of the charge on the repulsion, so that $c_1=1.20$ and $c_2=0.81$ and $c_{+-}=0.929$ is written c_0, one obtains for the total repulsive potential in the crystal,

$$\begin{aligned}B(r)&=bc_0[Mb_+b_-e^{-r/\rho}+\tfrac{1}{2}M'b_+^2c_1e^{-ar/\rho_+}\\ &\qquad+\tfrac{1}{2}M'b_-^2c_2e^{-ar/\rho_-}] \quad (9)\\ &=M_1(1+M_2^+ +M_2^-),\end{aligned}$$

$$M_1=Mbc_0b_+b_-e^{-r/\rho},$$

$$M_2^+=\frac{M'c_1b_+}{2Mb_-}e^{-(a/\rho_+-1/\rho)r},$$

$$M_2^-=\frac{M'c_2b_-}{2Mb_+}e^{-(a/\rho_--1/\rho)r}.$$

The constant a has the value 1.155, 1.414 and 1.633 for the CsCl, NaCl and Zincblend lattice, respectively. c_0, c_1 and c_2, the dependence of the repulsion on the charge are computed from a theoretical equation of Pauling's[8] assuming 18

[7] P. P. Ewald and C. Hermann, *Strukturbericht*, 1913–1928.

[8] L. Pauling, Zeits. f. Krist. **67**, 377 (1928).

electron shell positive ions and 8 electron shell negative ions. The values of the b_-'s are calculated from the alkali halides, and those of the b_+'s are later calculated in this paper. The constant b is arbitrarily chosen to be 10^{-12} erg.

M_2^+ represents the total repulsion due to pairs of Ag^+ ions divided by that due to Ag^+ halide pairs, and M_2^- the total repulsion of halide pairs divided by that of the Ag^+ halide pairs. M_2^+ at $r \geq r_0$ is entirely negligible for all silver salts and will be omitted from the further calculation.

For the thallium salts ρ is found to have very nearly the same value as in the alkali halides and the somewhat simpler equations of B.M. have been used throughout. The equations are equivalent to Eq. (9) setting $\rho = \rho_- = \rho_+$ and adding $M_2^+ + M_2^- = M_2$.

Using Eq. (9) one obtains for the derivatives,

$$\tau = -r_0 \frac{\partial B(r_0)}{\partial r} = \frac{r_0}{\rho} M_1[1 + yM_2^-], \qquad (10)$$

$$\sigma = r_0^2 \frac{\partial^2 B(r)}{\partial r^2} = \left(\frac{r_0}{\rho}\right)^2 M_1[1 + y^2 M_2^-], \qquad (11)$$

with

$$y = a\rho/\rho_-,$$

when M_1 and M_2^- are understood to be the values of these functions at $r = r_0$. This leads to the equation for r_0/ρ

$$r_0/\rho = (\sigma/\tau)[1 + (y - y^2)M_2^-/(1 + y^2 M_2^-)]. \qquad (13)$$

Table I includes many of the numerical steps of the calculations and the value of ρ, row 33. An average value, $\rho = 0.260 \times 10^{-8}$ cm and 0.361×10^{-8} cm for the silver and thallium salts, respectively, is obtained. The further calculations are made with these average values.

$B(r_0)$ the repulsive potential at $r = r_0$ may now be calculated from Eqs. (9) and (10),

$$B(r_0) = (1 - k)\tau(\rho/r_0), \qquad (14)$$

$$k = (y - 1)M_2^-/(1 + yM_2^-).$$

TABLE I. *Calculation of the theoretical lattice energies.*

1 Salt	AgF	AgCl	AgBr	AgI	TlCl	TlBr	TlI
2 Crystal type	NaCl	NaCl	NaCl	Zincblend	CsCl	CsCl	CsCl
3 Q_{00}^2 (neg. ion) $\times 10^{16}$ cm^2	1.44	3.40	4.08	5.27	3.40	4.08	5.27
4 ϵ (neg. ion) $\times 10^{12}$ ergs/molecule	19.0	15.6	13.9	11.0	15.6	13.9	11.0
5 α (neg. ion) $\times 10^{24}$ cm^3	1.15	3.45	4.47	7.29	3.45	4.47	7.29
6 α (pos. ion) $\times 10^{24}$ cm^3	1.72	1.72	1.72	1.72	3.50	3.50	3.50
7 $\Sigma\alpha \times 10^{24}$ (calc.) cm^3	2.87	5.17	6.19	9.01	6.95	7.97	10.79
8 $\Sigma\alpha$ (yellow) $\times 10^{24}$ (exp.) cm^3	——	5.41	6.58	9.54	——	——	——
9 $\Sigma\alpha$ ($\lambda = \infty$) $\times 10^{24}$ (exp.) cm^3	——	5.14	6.20	9.00	——	——	——
10 ϵ (pos. ion) $\times 10^{12}$ ergs/molecule	30.0	——	——	——	30.0	——	——
11 $c_{++} \times 10^{60}$ ergs $\times$ cm^6	67	——	——	——	268	——	——
12 $c_{--} \times 10^{60}$ " "	19	133	208	437	133	208	437
13 $c_{+-} \times 10^{60}$ " "	34.5	89	109	151	179	222	307
14 $d_{++} \times 10^{76}$ ergs cm^6	91	——	——	——	500	——	——
15 $d_{--} \times 10^{76}$ " "	23	268	475	1228	268	475	1228
16 $d_{+-} \times 10^{76}$ " "	44	150	199	315	346	460	720
17 S_6'	6.595	——	——	4.354	8.709	——	——
18 S_6''	1.807	——	——	0.762	3.545	——	——
19 S_8'	6.146	——	——	4.104	8.208	——	——
20 S_8''	0.800	——	——	0.253	2.147	——	——
21 $C \times 10^{60}$ ergs $\times$ cm^6	305	767	967	850	2270	2785	3930
22 $D \times 10^{76}$ ergs $\times$ cm^8	316	1065	1410	1467	3665	4820	7760
23 $r_0 \times 10^8$ cm	2.46	2.772	2.884	2.812	3.33	3.44	3.62
24 $\beta \times 10^6$ (compressibility) bars^{-1}	——	2.40	2.75	4.11	4.9	5.3	——
25 $V^{-1}(\partial V/\partial T)_p \times 10^6$	——	98.9	104	——	——	——	——
26 $9V/N\beta \times 10^{12}$ ergs/molecule	——	159	156	150	104	106	——
27 $(3T/N\beta)(\partial V/\partial T) \times 10^{12}$ ergs/molecule	(1.50)	1.57	1.63	(1.70)	(1.60)	(1.70)	(1.80)
28 $\alpha e^2/r_0 \times 10^{12}$ ergs/molecule	16.20	14.39	13.82	13.29	12.04	11.66	11.09
29 $C/r_0^6 \times 10^{12}$ " / "	1.39	1.70	1.60	1.74	1.66	1.67	1.75
30 $D/r_0^8 \times 10^{12}$ " / "	0.24	0.32	0.29	0.38	0.24	0.25	0.34
31 $\tau \times 10^{12}$ " / "	24.9	25.6	24.6	25.1	22.3	22.0	22.5
32 $\sigma \times 10^{12}$ " / "	——	283.	276.	277.	215.	217.	——
33 σ/τ	——	11.3	10.8	11.0	9.64	9.90	——
34 $\rho \times 10^8$ cm	——	0.247	0.271	0.260	0.356	0.366	——
35 r_0/ρ calculated	9.45	10.65	11.09	10.78	9.21	9.51	10.03
36 $B(r) \times 10^{12}$ ergs/molecule	2.63	2.38	2.20	2.28	2.36	2.23	2.14
37 $\frac{1}{2}h\nu$ " / "	0.10	0.08	0.06	0.05	0.06	0.05	0.04
38 $U \times 10^{12}$ ergs/molecule	15.10	13.95	13.53	13.08	11.52	11.30	11.00
39 U k cal.	219	203	197	190	167	164	159

TABLE II. *Calculation of the experimental lattice energies. ΔH in kilocalories of the reactions.**

Reaction		AgF	AgCl	AgBr	AgI	TlCl	TlBr	TlI
$MX_{cr.}$ 0°K→$MX_{cr.}$	291°K	2.5	2.8	2.9	3.0	2.9	3.1	3.2
$MX_{cr.}$→$M_{s.s.}+\frac{1}{2}X_{2\,s.s.}$	291°K	48.7	30.6	23.7	14.9	48.7	41.1	30.1
$\frac{1}{2}X_{2\,s.s.}$→$X_{g.}$	291°K	31.8	28.8	26.7	25.5	28.8	26.7	25.5
$X_{g.}$ 291°K→$X_{g.}$ 0°K		−1.1	−1.1	−1.1	−1.1	−1.1	−1.1	−1.1
$X_{g.}+e^-$→$X_{g.}^-$ 0°K		−95.3	−86.5	−81.5	−74.2	−86.5	−81.5	−74.2
$M_{cr.}$ 291°K→$M_{cr.}$ 0°K		−1.7	−1.7	−1.7	−1.7	−1.7	−1.7	−1.7
$M_{cr.}$→$M_{g.}$ 0°K		59.0	59.0	59.0	59.0	39.0	39.0	39.0
$M_{g.}$→$M_{g.}^+ + e^-$ 0°K		173.8	173.8	173.8	173.8	140.0	140.0	140.0
Sum = $MX_{cr.}$→$M_{g.}^+ + X_{g.}^-$ 0°K		217.7	205.7	201.8	199.2	170.1	165.6	160.8
Theoretical lattice energy		219	203	197	190	167.	164.	159.
Difference		−1.3	2.7	4.8	9.2	2.9	1.6	1.3

* Subscripts, cr. indicate crystal; s.s., standard state; and g, gas.

The complete lattice energy U is given by

$$-U=\Phi_0=-\frac{\alpha e^2}{r_0}-\frac{C}{r_0^6}-\frac{D}{r_0^8}+B(r_0)+\tfrac{1}{2}h\nu_0, \quad (15)$$

the small value of $h\nu_0/2$ can be easily estimated. The values of the lattice energy in ergs per molecule and in k cal. are tabulated in the last two rows of Table I.

In Table II are given the energies of the reactions used to calculate what is called the experimental lattice energies. The heats of formation of the crystals are taken from *International Critical Tables*, as are also the heats of formation of the halogen gaseous atoms. The small energy changes between 291°K and 0°K are all estimated. The electron affinity of the halogen atoms is taken from a paper by Mayer and Helmholz[9] where they were calculated from the lattice energies of the alkali halides. The heat of sublimation of the metals has been estimated by the use of the Hildebrand[10] modification of Trouton's rule. The sum of the ΔH's of all of the first eight reactions give the ΔH, which at 0°K is the ΔE, of the dissociation of the crystal into gaseous ions, the lattice energy. The theoretical lattice energy and the difference between the two values is also tabulated.

The uncertainties in the lattice constants and in the compressibilities may account for 1 k cal. uncertainty in the theoretical lattice energies. The van der Waals potentials of about 20 k cal. may be in error by as much as 6 k cal., which would contribute about 3 k cal. error to the lattice energy calculations. In all the values of the theoretical lattice energy may be in error by about 4 k cal. as an upper limit, even if the assumptions under which they are calculated hold exactly. The experimental lattice energies may also be in error by as much as 3 or 4 k cal., but the difference between the values for different halides of the same positive ion are not likely to be in error by more than 2 k cal. The trend of 6 k cal. in the difference between the theoretical and experimental energies from fluoride to bromide of the silver salts is probably real, and represents a deviation from a purely ionic character. The trend could be diminished by assuming a greater polarizability for the Ag^+ ion, or in general by changes in the assumptions tending to increase the van der Waals potential; but it seems probable that this trend shows an increasing homopolar contribution to the lattice energy which is zero for the fluoride and about 2 or 3 percent of the total energy in the bromide.

This view is strengthened by the marked difference between the theoretical and experimental energies in the silver iodide. It seems that there is no doubt that this difference cannot be explained by errors in the choice of the van der Waals potential. Further evidence will be deduced later in this paper to show that the homopolar bond contributes approximately 10 percent of the total experimental lattice energy.

The thallium halides on the other hand, are seen to be all, within the accuracy of these calculations, purely ionic.

THE LATTICE CONSTANT

The Eqs. (7) and (8) assume that the repulsive potential between any two ions i, j, can be calculated from constants of the ions, b_i, b_j, ρ_i,

[9] J. E. Mayer and L. Helmholz, Zeits. f. Physik **75**, 16 (1932).

[10] J. H. Hildebrand, J. Am. Chem. Soc. **37**, 970 (1915).

TABLE III. *Values of theoretical lattice constants.*

	AgF	AgCl	AgBr	AgI	TlCl	TlBr	TlI
Value of b_-	26.80	77.4	105.3	189.5	77.4	105.3	189.5
Value of b_+	187.8	187.8	187.8	187.8	33.78	33.78	33.78
Calculated $r_0\times10^8$ cm	2.45	2.78	2.89	2.952	3.30	3.42	3.69
Experimental $r_0\times10^8$ cm	2.46	2.772	2.884	2.812	3.33	3.44	3.62
Difference, $\delta r\times10^8$ cm	−0.01	0.01	0.01	0.14	−0.03	−0.02	+0.07

ρ_j, and c_{ij} the dependence on charge and outer electron configuration. Actually the method used here and in B.M. does not do this. The constant ρ is indeed calculated from several crystals and an average value chosen for the repulsive potential, but the product b_ib_j is implicitly determined for each crystal by the use of the lattice constant. The ratio b_i/b_j does enter the equations used, but in such an unimportant way (in the computation of the small M_2^+ and M_2^-) that in the calculation of the lattice energies of the alkali halides the Goldschmidt radii were used to estimate the ratio, and no attempt was made, or needed, to justify this, except in a most qualitative way.

Huggins and Mayer[11] have shown that 9 values of b for the 9 ions of the alkalis and halides can be so chosen that one can calculate the 20 lattice constants of the 20 alkali halides to within about 0.01A, probably within the experimental error of their determination.

That is, Eq. (7) is justified experimentally for the purely ionic alkali halides. With the values of b_- for the halides found from the alkali halides, the values of b_+ for Ag^+ and Tl^+ may be calculated. One will obtain 4 values from the 4 halides for Ag^+, and 3 values from the 3 halides for Tl^+. The values of b for Tl^+ are found to have a slight trend, which is probably of significance but will be ignored, and the average of all used to obtain b for Tl^+. The values of the b for Ag^+ decrease noticeably with increasing atomic number of the negative ion. Assuming that the salts AgF and AgCl are essentially ionic, the true b_+ for Ag^+ may be taken as an average of that determined from these two salts. (The lattice constant of AgF is sufficiently uncertain to warrant the use of AgCl although it may be somewhat homopolar.)

With these average values of b for Ag^+ and Tl^+ the lattice constants of the salts may be calculated. The results are tabulated in Table III. For the thallium salts although the calculated lattice constants do not agree well with the experimental values, the differences are probably not much greater than the experimental uncertainty in the lattice constants, which are not well known. A trend is apparent in the differences. For the silver salts the trend is decided and large. The calculated theoretical lattice constant for AgI is considerably higher than the experimental.

This small experimental lattice constant is in good agreement with the observations on the lattice energy for AgI. A homopolar bonding potential is probably pulling the ions closer together and simultaneously lowering the energy. We may regard the calculated lattice constant as the lattice constant of a purely ionic crystal. The lower experimental lattice constant is due to an actual existent homopolar binding in addition to the ionic.

One may now compute more exactly the homopolar part of the potential in AgI. The repulsive potential in Table I has been calculated from the empirical lattice constant of the crystal. Using instead the value of b for Ag^+ found from the fluoride and chloride one may calculate the repulsion in a truly ionic crystal. This truly ionic crystal would have the lattice energy 184 k cal. at its equilibrium lattice constant 2.95A, and 178 k cal. at the experimental lattice constant 2.81A, corresponding to the highly compressed crystal. Subtracting this from the experimental lattice energy one arrives at a value 21 k cal., or 10 percent, which is due to the existence of a homopolar potential.

The actual calculations of the b_+'s and the lattice constants are not reproduced here in detail. By using Eq. (9) and the value of $B(r)$ at $r=r_0$ given in Table I, b_+ can be calculated if b_- is known. Having an average value of b_+ the value of $B(r)$ at $r=r_0$ can be recalculated. In order to calculate the theoretical lattice constant with the

[11] M. L. Huggins and J. E. Mayer, Phys. Rev. **43**, 373A (1933). Abstract of Report at Atlantic City Meeting, December, 1932.

new theoretical value of the repulsion $B(r)$ one seeks a value of r that will satisfy Eq. (5). By using a method of variations the following approximation is obtained. If b_0 is the average b which we have chosen as the correct b of the positive ion, and b_e the experimental value previously determined from the lattice constant of the crystal, one finds for δr, the difference between the theoretical lattice constant and the experimental:

$$\delta r = \rho(\omega - 1)/(9V/N\beta\sigma) \qquad (16)$$

with

$$\omega = b_0/b_e.$$

The Stability of Different Lattice Types

In the previous discussion it has been assumed that insofar as the compounds studied are purely ionic and not in such a crystal that the ions are not deformed (which means that one is restricted to regular crystals), the complete potential between any two ions is known as a function of the distance between them. In principle one can then calculate the lattice energy of any regular crystal lattice for these compounds. The actual work of solving for the equilibrium lattice constant r_0 out of Eq. (5) would be somewhat tedious.

It is, however, comparatively simple to obtain the change of energy with change of lattice type at constant r_0, and the change of energy with r of the new hypothetical lattice, as it adiabatically expands or contracts to its equilibrium r_0 can be easily estimated. The method is that used on the alkali halides in the paper B.M. For each term, except the $h\nu_0/2$, of the expression for the lattice energy, Eq. (15), one may calculate the change in the value of that term due only to a change in the lattice type, but with r_0 held constant. The sum of these changes will give the complete variation $(\delta\Phi)_{r=r_0}$ in the lattice potential with change of crystal type at constant r_0. The small term, invariable negative, corresponding to the decrease in lattice potential, $\frac{1}{2}(\partial^2\Phi/\partial r^2)(\delta r)^2$, as the new lattice type changes to its equilibrium density, is then added. Starting always from the experimental type a net positive value for the total $\delta\Phi$ indicates that the calculation shows the hypothetical lattice type to be instable. A net negative $\delta\Phi$ indicates an error of some sort in the calculation, provided the hypothetical lattice type is not actually experimentally obtained. In Table IV the results of such a calculation are shown.

It is to be seen that AgF, AgCl and AgBr are calculated to be instable as Zincblend or CsCl lattices, and should, as they do, crystallize in rocksalt lattices. AgI, on the other hand is calculated to be stable in the rocksalt lattice, which is in contradiction to the experimental evidence. The discrepancy of 0.43×10^{-12} erg or 6 k cal. is far too large to be accounted for by anything but a failure of the fundamental assumption that it is ionic. The salts TlCl and TlBr are found to be stable as rocksalt lattices, although they actually crystallize in the CsCl lattice. Here, however, the discrepancy of 0.02 and 0.01×10^{-12} erg is so small that it is easily accounted for by a relatively small error in the van der Waals potential. TlI is found to be stable in the CsCl type lattice.

Table IV. *Calculation of potential energy change with change of lattice type.* Energies in 10^{-12} erg/molecule.

Salt	Experimentally stable lattice	Hypothetical lattice	Change at constant r_0 of				$\frac{\partial^2\Phi}{\partial r^2}\frac{(\delta r)^2}{2}$	$\delta\Phi$
			$-\alpha\epsilon^2/r_0$	$-C/r_0^6$	$-D/r_0^8$	$B(r_0)$		
AgF	Rocksalt	Zincblend	+1.02	+0.55	+0.09	−0.95	−0.13	+0.58
AgCl	"	"	+0.90	+0.67	+0.13	−0.96	−0.13	+0.61
AgBr	"	"	+0.87	+0.67	+0.11	−0.93	−0.13	+0.49
AgI	Zincblend	Rocksalt	−0.89	−1.23	−0.26	+2.08	−0.13	−0.43
AgF	Rocksalt	CsCl	−0.14	−0.67	−0.12	+1.16	−0.06	+0.17
AgCl	"	"	−0.12	−0.82	−0.16	+1.72	−0.06	+0.56
AgBr	"	"	−0.12	−0.81	−0.15	+1.99	−0.06	+0.85
TlCl	CsCl	Rocksalt	+0.10	+0.56	+0.09	−0.73	−0.04	−0.02
TlBr	"	"	+0.10	+0.55	+0.08	−0.70	−0.04	−0.01
TlI	"	"	+0.09	+0.57	+0.11	−0.70	−0.04	+0.03

Discussion of the Results

The salts here considered all show two distinct variations from the characteristics of the definitely ionic alkali halides. Their lattice energies are markedly high, which is qualitatively evidenced by their low solubilities, and their lattice constants do not increase as rapidly with increasing halide atomic number as do the alkalis. The difference in lattice constant of AgF and AgBr is 0.42A as compared with 0.67A for the difference between NaF and NaBr. The difference $r_0(\text{TlCl}) - r_0(\text{TlI})$ is 0.29A. Compared with 0.39A for CsCl and CsI.

A high attractive van der Waals potential, increasing with the size of the negative ion, and in the case of the silver salts a low repulsive exponent ρ deducable from their low compressibilities, qualitatively explain both of these anomalous characteristics. In the case of the three salts AgF, AgCl and AgBr the explanation is satisfactory quantitatively. There is some evidence that AgBr is not entirely ionic, as one would expect if AgI is supposed to have an appreciable homopolar potential, but it would be possible to account for the deviations from the calculations by assuming a somewhat greater van der Waals potential. AgI, however, cannot be accounted for quantitatively as ionic. Not only are the deviations from the lattice energy and constant too great to be patched by a small alteration of the assumed polarizabilities and frequencies, but more important, it crystallizes in the wrong type lattice. Were it ionic, and especially if the van der Waals potential were larger, it would be instable in the zincblend lattice, (and also in the similar Wurtzite lattice). The homopolar potential apparently favors markedly the low coordination number type of lattice, which is probably to be expected.

The quantitative calculation of the TlCl, TlBr and TlI lattice energies is satisfactory. The anomalous lattice constants are not accounted for successfully, although the experimental values are sufficiently uncertain to allow some latitude. The calculated lattice constants would agree better with the experimental, as would also the lattice energies, were the van der Waals potential assumed to be greater, particularly for the iodide. Here the study of the stability of different types corroborates the idea that the van der Waals potential is higher than that used. A higher van der Waals potential is needed to account for the experimental stability of the CsCl type lattice, whereas an existent homopolar potential would be expected to favor the lower coordination number of the rocksalt lattice. The author considers this a strong reason for believing that practically no homopolar binding is present in these salts.

Some Conclusions from Rules on the Concentration of Valency Electrons in Binary Intermetallic Alloys

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1. INTRODUCTION

IN 1926 W. Hume-Rothery suggested that the similarity of β-phases in Cu–Zn, Ag–Zn, Au–Zn, Ag–Cd, Au–Cd, Cu–Al, Ag–Al and Cu–Sn alloys is due to the fact that these phases are space lattices of atoms and electrons for which the ratio of electrons to atoms, the so-called concentration of valency electrons, is the same, viz., 3 : 2, according to the chemical formulae CuZn, AgZn, AuZn, AgCd, AuCd, Cu_3Al, Ag_3Al and Cu_5Sn which are usually ascribed to these β-phases.[1] At the same time, from a survey of displacements of homogeneity ranges of structurally similar phases in certain binary alloys of copper, silver and gold Arne Westgren and Gösta Phragmén concluded too that the atomic grouping of intermetallic phases is to a considerable degree regulated by their concentration of valency electrons.[2]

2. STATEMENT OF THE RULES

To-day 35 binary intermetallic alloys are known in which up to three intermediate phases are met with which are structurally similar to β-, γ- and ϵ-phases of the Cu–Zn-system.[3] As a rule these phases occur at such compositions for which the concentrations of valency electrons attain certain values peculiar to each type of structure. The characteristic values for concentrations of valency electrons are:

(1) 3 : 2 for phases with the body-centered cubic lattice of β-brass or with the cubic lattice of β-manganese with 20 atoms in the unit cube, phases which will be referred to as β-phases.

(2) 21 : 13 for phases with the cubic lattice of γ-brass with 52 atoms in the unit cube, phases which will be referred to as γ-phases.

(3) 7 : 4 for phases with the close-packed hexagonal lattice of ϵ-brass, phases which will be referred to as ϵ-phases.

3. FORMULAE FOR AND FROM THE RULES

Now, if the number of valency electrons of the first component of the binary alloy is denoted by m, and that of the second one by n; if in the phases with β-, and γ-, and ϵ-structures the number of atoms of the first component is denoted by x, and that of the second one by y, then the concentration of valency electrons, k, is defined by $(mx+ny) : (x+y) = k$. Solving this equation with respect to the ratio x/y, we have $x : y = (k-n) : (m-k)$. In this expression the left-hand side is positive, and therefore the right-hand side should be positive too. But that necessitates that m, n, and k should satisfy the inequality $m \leqq k \leqq n$.

4. CONCLUSIONS FROM THE INEQUALITY

The obtained inequality leads to following conclusions:

(1) β-, γ-, and ϵ-structures are not to be expected in binary intermetallic alloys if both components have the same number of valency electrons.

(2) A β-, γ- or ϵ-structure is to be expected in binary intermetallic alloys if the one component has less and the other component more than

[1] J. Inst. Met. **35**, 295 (1926), London.

[2] Ark. mat., astron. och fysik **B19**, 5 (1926).

[3] Arne Westgren und Gösta Phragmén, Zeits. f. Metallkde. **15**, September (1926); Metallwirtsch. **7**, 701–702 (1928); Zeits. f. anorg. allg. Chemie **175**, 84 (1928); Zeits. f. Metallkde. **18**, 279 (1929); Trans. Faraday Soc. **25**, 380–382 (1929). A. Westgren und W. Eckman, Ark. kem., mineral. och geol. **B10**, No. 11, 1–4 (1930). W. Eckman, Zeits. f. physik. Chemie **B12**, 58–59, 77 (1931). A. Westgren, Zeits. f. Metallkde., No. 11 (1930); Metallwirtsch. **9**, 922–923 (1930); Trans. Amer. Inst. min. metallurg. Engr. Institute of Metals Div. 1931 p. 35–37; J. Frank. Inst. **212**, 592–595 (1932); Zeits. f. angew. Chem. **45**, 11, 13, 15–18 (1932); Harald Perlitz, Acta et Commen. Univ. Tartuensis, **24**, tract No. 3 (1932); Metallwirtsch. 12 (1933).

3 : 2, 21 : 13 or 7 : 4 valency electrons, respectively.

(3) Since the characteristic values of concentrations of valency electrons are between two consecutive integers, it follows that in alloys in which one of the three structures referred to is met with, both other structures should be expected too. This statement accounts for the frequent coexistence of β-, γ-, and ϵ-structures.

(4) Since the lower and upper limit for the values of concentration of valency electrons are one and two, it follows that a β-, γ- or ϵ-structure is to be expected in binary intermetallic alloys if the one component has not more than one valency electron, and the other component has not less than two valency electrons.

The Dipole Moments of Some Mercaptans and Sulfides

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The dipole moments of thianthrene, two thioethers and two mercaptans are measured and compared with values in the literature. The differences in moment of corresponding oxygen and sulfur compounds are attributed to inherent differences in the H–O, C–O, H–S and C–S moments and to the greater polarizability of sulfur as compared to oxygen. In contrast to the oxygen ethers, the thioethers show as much intermolecular action as the mercaptans.

THIS investigation was undertaken some time ago with the object of comparing the mercaptans and sulfides, for certain of which approximate moments had been calculated previously,[1] with the corresponding oxygen compounds, which had shown unusual dielectric behavior.[2] Hunter and Partington, who determined the dipole moments of ethyl mercaptan and ethyl sulfide some little time ago,[3] have just published values for thiophenol, two alkyl mercaptans, and three more sulfides,[4] and have given an interesting discussion of their results. Although their values for the sulfides are in excellent agreement with those in the present paper, as will shortly be seen, there is a marked discrepancy in the values for the mercaptans, which are difficult to obtain in a very pure state. On this account an unusually detailed description of the criteria of purity of the two mercaptans here measured seems desirable.

PURIFICATION OF MATERIALS

Benzene

Mallinckrodt's (Thiophene Free) analytical reagent grade benzene was treated as in earlier work.[5]

Thianthrene

Material very kindly loaned by Professor Gregg Dougherty (m.p. 156.5–157.5°) was fractionally crystallized nine times from pure dry benzene and dried in an evacuated desiccator. This material was odorless and concentrated solutions in benzene showed no coloration; m.p., 157.5–157.8°. Bergmann and Tschudnowsky report[6] their material to melt at 154°.

Ethyl sulfide

Material from the Eastman Kodak Company was extracted with sodium hydroxide solution, washed several times with water, shaken with mercury (no decoloration), dried for several days with anhydrous sodium sulfate, decanted and twice fractionally distilled; b.p., 91.8° (756 mm); n_D^{20} 1.44265; n_D^{25} 1.4400.

n-Amyl sulfide

Material from the Eastman Kodak Company was treated in the same way as the ethyl sulfide and twice fractionally distilled under reduced pressure; b.p., 103–103.5° (13 mm); n_D^{20} 1.45547; n_D^{25} 1.45377.

n-Butyl mercaptan

Material from the Eastman Kodak Company was dried for several days with anhydrous sodium sulfate and fractionally distilled in an apparatus filled with nitrogen. The boiling point was constant at 97.5° (760 mm) during the collection of the first three fractions, after which it rose 0.1°. A 240 cc sample was collected in seven fractions

[1] C. P. Smyth, J. Am. Chem. Soc. **46**, 2151 (1924).
[2] C. P. Smyth and W. N. Stoops, J. Am. Chem. Soc. **51**, 3312, 3330 (1929).
[3] E. C. E. Hunter and J. R. Partington, J. Chem. Soc. **1931**, 2062.
[4] E. C. E. Hunter and J. R. Partington, J. Chem. Soc. **1932**, 2812, 2819.
[5] C. P. Smyth and W. S. Walls, J. Am. Chem. Soc. **54**, 1854 (1932).
[6] E. Bergmann and M. Tschudnowsky, Ber. **65**, 457 (1932).

in the quantities given below with the following refractive indices: (1) 50 cc, n_D^{20} 1.4381; (2) 40 cc, n_D^{20} 1.4381, n_D^{25} 1.4356; (3) 35 cc, n_D^{20} 1.4381; (4) 50 cc, n_D^{20} 1.4387; (5) 25 cc, n_D^{20} 1.4402; (6) 20 cc, n_D^{20} 1.4416. The second fraction, which was used for preliminary dielectric constant and density measurements, had an index considerably lower than the value 1.4411 found by Hunter and Partington and a density, 0.8377, obtained by extrapolation to 20°, also lower than the value 0.8397 found by Hunter and Partington and the value 0.8412 obtained from the specific volume determined by Bingham and Fornwalt.[7] The density of this second fraction was, however, slightly higher than the value 0.836 given in *International Critical Tables* and its boiling point 97.5° was between the value 98° given by *International Critical Tables* and the value 97.2° found by Hunter and Partington.

In order to remove possible butyl alcohol, fractions 1 and 4 combined were washed five times with distilled water, dried with anhydrous sodium sulfate, further dried with phosphorus pentoxide for a few hours, decanted, and fractionally distilled as before; b.p., 97.9° (755 mm); n_D^{20} 1.44275; n_D^{25} 1.44025; d_4^{20} 0.8415. These constants are in excellent agreement with those recently published by Ellis and Reid.[8]

As this sample appeared to be purer than the first material measured, it was used to obtain the data given in this paper. The dipole moment obtained for it was 0.04×10^{-18} lower than that found for the first sample.

n-Amyl mercaptan

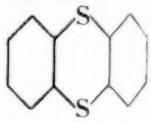
Material from the Eastman Kodak Company was dried for several days with anhydrous sodium sulfate, decanted, and fractionally distilled three times; b.p., 123.7–124.0° (756 mm); n_D^{20} 1.4459; n_D^{25} 1.44386. The density, 0.8418, obtained by extrapolation to 20°, is in excellent agreement with the value 0.8415 of Bingham and Fornwalt, but much lower than the value 0.857 in *International Critical Tables*, which gives a somewhat lower refractive index, 1.4437, and a higher boiling point 126°. Our values are in agreement with the values d_4^{25} 0.8375 and n_D^{25} 1.4440 obtained by Ellis and Reid.

Experimental Results

The densities d and dielectric constants ϵ of the polar substances of mole fraction c_2 in solution in benzene were measured with the apparatus and methods previously employed,[9] a wave-length of 1000 meters being used in the dielectric constant determinations. The results are shown in Table I, in which the values opposite $c_2=0$ for the benzene-thianthrene mixtures are for the pure benzene used in all the measurements. $P_2=(\epsilon-1)M/(\epsilon+2)d$ has been extrapolated to $c_2=0$ in the usual manner to obtain P_∞, from which, together with the molar refraction MR_D, the moment is calculated as $\mu=0.0127\times10^{-18}[(P_\infty-MR_D)T]^{\frac{1}{2}}$. The values are summarized in Table II, and the moments of the mercaptans and sulfides are shown in Table III marked "W. and S." together with the values of Hunter and Partington in the column marked "H. and P."

Discussion of Results

The moment, 1.41×10^{-18}, found for thianthrene is decidedly lower than the value, 1.68×10^{-18}, just published by Bergmann and Tschudnowsky[6] but surprisingly high for the structure, indicating, as Bergmann and Tschudnowsky conclude, that the rings do not lie in the same plane. Indeed, a considerable folding of the structure about the two sulfurs must occur in order to give such a moment, for the C–S valences must act at such angles as partially to oppose one another's moments. The reason for the discrepancies in the values for thianthrene and the mercaptans is presumably the difficulty of purification, but it is believed that the materials finally used in the present investigation are reliable as to purity. Impurity should account for the difference found by Hunter and Partington between the higher mercaptan and the ethyl compound, the value for which is nearer than the others to the values found in the present work for the higher compounds.



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[8] L. M. Ellis, Jr., and E. E. Reid, J. Am. Chem. Soc. **54**, 1674 (1932).

[9] C. P. Smyth and W. S. Walls, J. Am. Chem. Soc. **53**, 527 (1931).

TABLE I. *Dielectric constants, densities and polarizations.*

c_2	ϵ 25°	ϵ 50°	d 25°	d 50°	P_2 25°	P_2 50°
			Benzene-thianthrene			
0.00000	2.276	2.226	0.8730	0.8461	(26.68	26.76=P_1)
.00624	2.301	2.249	.8782	.8514	106.8	103.7
.01051	2.318	2.264	.8817	.8549	106.6	103.8
.01053	2.318	2.264	.8816	.8549	107.4	103.7
.01199	2.324	2.270	.8828	.8561	106.8	104.3
.01351	2.330	2.275	.8840	.8572	107.4	104.5
.01701	2.342	2.288	.8868	.8600	105.5	104.4
.01761	2.344	2.289	.8872	.8605	105.6	103.4
			Benzene-ethyl sulfide			
0.01815	2.334	2.278	0.8717	0.8449	79.6	76.9
.03496	2.389	2.326	.8711	.8443	79.0	76.3
.05603	2.458	2.386	.8700	.8432	78.8	75.7
.10292	2.615	2.523	.8677	.8410	78.2	75.2
.33000	3.358	3.183	.8572	.8310	73.5	71.7
.50070	3.946	3.705	.8498	.8239	71.5	70.0
.60390	4.313	4.002	.8457	.8197	70.2	68.7
1.00000	5.723	5.236	.8312	.8056	66.3	65.5
			Benzene-*n*-amyl sulfide			
0.01269	2.315	2.261	0.8717	0.8451	107.9	105.6
.02397	2.349	2.291	.8705	.8441	108.0	105.2
.03627	2.384	2.322	.8692	.8430	107.7	104.8
.09009	2.531	2.453	.8643	.8395	106.8	103.9
.14166	2.665	2.568	.8606	.8362	106.7	103.5
.28299	2.956	2.832	.8526	.8296	104.6	102.2
.46309	3.244	3.088	.8460	.8244	103.0	100.8
1.00000	3.826	3.594	.8356	.8162	101.1	99.0
			Benzene-*n*-butyl mercaptan			
0.02771	2.353	2.294	0.8714	0.8446	72.9	70.4
.05204	2.421	2.355	.8703	.8436	72.4	70.2
.07853	2.498	2.423	.8686	.8421	72.7	70.3
.13773	2.666	2.571	.8659	.8396	71.6	69.4
.22957	2.925	2.803	.8617	.8358	70.2	68.3
.37172	3.315	3.142	.8562	.8304	67.9	66.2
.56844	3.847	3.611	.8492	.8239	65.4	64.1
1.00000	4.952	4.586	.8368	.8123	61.2	60.4
			Benzene-*n*-amyl mercaptan			
0.02123	2.337	2.280	0.8718	0.8451	79.0	76.7
.02965	2.362	2.302	.8712	.8444	79.6	77.0
.05362	2.427	2.361	.8698	.8432	78.2	76.0
.06427	2.460	2.387	.8692	.8427	78.8	75.9
.13816	2.663	2.567	.8652	.8392	77.2	74.8
.21759	2.877	2.753	.8612	.8357	76.0	73.6
.23514	2.914	2.789	.8603	.8350	75.3	73.1
.40585	3.337	3.158	.8535	.8291	73.0	71.0
.51977	3.600	3.388	.8493	.8255	71.7	69.9
1.00000	4.547	4.230	.8373	.8145	67.4	66.3

TABLE II. *Refractions, orientation polarizations and dipole moments.*

	MR_D	$P_\infty - MR_D$ 25°	$P_\infty - MR_D$ 50°	$\mu\times10^{18}$ 25°	$\mu\times10^{18}$ 50°
Thianthrene	65.9	41	38	1.41	1.41
Ethyl sulfide	28.57	51.7	48.2	1.58	1.58
n-Amyl sulfide	56.44	51.9	48.8	1.58	1.59
n-Butyl mercaptan	28.40	45.4	42.8	1.48	1.49
n-Amyl mercaptan	33.03	47	44	1.50	1.51

TABLE III. *Dipole moments of sulfides and mercaptans* ($\times10^{18}$).

Hydrogen sulfide 0.93*

	Mercaptan W. and S.	*Mercaptan* H. and P.	*Sulfide* W. and S.	*Sulfide* H. and P.
Methyl				1.40
Ethyl		1.39	1.58	1.57
Propyl		1.33		1.55
Butyl	1.48	1.32		1.57
Amyl	1.50		1.58	

* J. B. Miles and C. T. Zahn, Phys. Rev. **32**, 497 (1928).

Hunter and Partington have based a fairly satisfactory calculation of the moments of the sulfides and the mercaptans upon the assumption of a 90° sulfur valence angle. A fairly satisfactory result is also obtained by using the 146° valence angle and the high $m_{C-H}+m_{C-S}$ moment, 2.5×10^{-18}, calculated by Smyth and Walls.[10] The moment, 1.46×10^{-18}, thus calculated for the sulfides is very close to the experimentally determined values in Table III. However, as pointed out by Smyth and Walls, this large sulfur valence angle and surprisingly high C–S moment are dependent upon a somewhat inaccurate value in the literature for the moment of p-$ClC_6H_4SC_6H_5$ and upon the assumption that the moment of the para-substituted group is approximately independent of the other moments in the molecule. The differences between the moments of para-substituted phenols, anisoles, etc.,[10] make it appear probable that this assumption is not generally justifiable in the case of the ethers and thioethers, thus leaving the question of the sulfur valence angle open as far as dipole moments are concerned.

Hunter and Partington have explained the differences between the moments of corresponding oxygen and sulfur compounds largely in terms of the considerable difference in polarizability of oxygen and sulfur, as was done roughly for water and hydrogen sulfide by Smyth.[1] A C–S moment inherently larger than the H–S and a C–O inherently smaller than the H–O, both of which probable facts are influenced by the sulfur and oxygen polarizabilities, can account for the differences in moment. Not only the increase in moment from the hydrogen halides to the

[10] C. P. Smyth and W. S. Walls, J. Am. Chem. Soc. **54**, 3230 (1932).

corresponding methyl halides, but, to a smaller extent, also the increase of the methyl halide to the corresponding ethyl compound increases with increasing polarizability of the halogen. It thus appears reasonable that, although the C–O moment is smaller than the H–O, the C–S moment should be larger than the H–S, which gives the mercaptans higher moments than H_2S and the sulfides higher moments than the mercaptans.

A surprising effect is apparent in the dependence of the observed polarization of the sulfide upon concentration. The highly associated alcohols show a strong and complicated dependence of apparent polarization upon concentration because of the strong effects of the H–O dipoles upon one another,[11] while the ethers show a polarization independent of concentration, presumably because the alkyl groups screen the C–O dipoles in adjacent molecules from one another. As would be expected, the supposedly unassociated mercaptans show (see Table I) a change of only 10 to 15 units of observed polarization between the pure liquid and the substance at infinite dilution, the difference from the behavior of the alcohols presumably being due to the partial screening of the H–S dipole by the structure of the sulfur atom. The sulfides in Table I, however, show a dependence of polarization upon concentration which, when the difference in molecular size is taken into account, is as great as that of the mercaptans. Thus, the ethyl sulfide molecule, which is approximately the same size as that of butyl mercaptan, increases in apparent polarization from the pure liquid to infinite dilution, 14.0 at 25° and 11.3 at 50°, while butyl mercaptan increases 12.6 at 25° and 10.8 at 50°. It appears possible that the larger size of the sulfur atom as compared to the oxygen prevents complete screening of the C–S dipoles by the alkyl groups so as to permit a larger external field than in the case of the oxygen ethers and consequently some molecular interaction. The larger moments of the sulfides are also a factor, possibly, helping to make the intermolecular action of the sulfides as large as that of the mercaptans.

[11] C. P. Smyth, *Dielectric Constant and Molecular Structure*, p. 180, The Chemical Catalog Company, Inc., New York, 1931.